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Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

CHLORINATION OF Zn-Pb-Cu-Ag-Fe SULPHIDE CONCENTRATES EMPLOYING SUBMERGED-LANCE CHLORINE INJECTION

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Dry Way Chlorination-Oxidation Process

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by

P. Pint* and V.M. McNamara*

SUMMARY

Technical feasibility has been shown and some operating parameters optimized for a pyrometallurgical (T = 500 to 800°C) chlorination process applicable to the treatment of sulphide concentrates. The chlorination steps are part of an overall flowsheet designed to recover zinc, lead, copper, silver and sulphur from complex New Brunswick sulphide concentrates. The conclusions derived from bench-scale experiments and from theoretical calculations are:

(1) Brunswick bulk sulphide concentrates can be readily and efficiently chlorinated to yield a liquid metal chloride product.
(2) The recovery of the metals in the melts can be >95%.
(3) Good quality sulphur can be produced.
(4) The resulting fluid metal chloride can be contained and is transported by gravity. No build-up of gangue materials occurs as the latter are dispersed throughout the melt.
(5) No energy input is required. The process is autogeneous.
(6) Production of S_xCl_y and Fe_yCl_{3y} can be minimized.
(7) Fuming of metal chloride(s) can be controlled.

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Experimental results and theoretical calculations evolved from this study are expected to assist in the evaluation and development of new chlorination methods (e.g., flash burner chlorination) and may be applied to the development of extraction and refining techniques for other metal sulphides, metals and metal oxides.

A flowsheet for a functional pyrometallurgical process and a novel reactor design are described.

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INTRODUCTION

Complex fine-grained zinc, lead, copper, iron sulphide ores occur in many countries throughout the world. Within Canada significant deposits are found in New Brunswick, Ontario, Manitoba, British Columbia and the Yukon. Although in some cases the average ore grade is relatively high, the economic exploitability has been hampered by the complex and very fine-grained structures of the deposit, which has made the production of a readily saleable concentrate difficult. For the New Brunswick deposits, CANMET (1) has demonstrated that metal recoveries greater than 90% can only be achieved if a bulk concentrate is produced. These complex concentrates, because of their relatively low grade, are not readily amenable to conventional metallurgical metal-extraction processes.

CANMET has been evaluating four options for processing the zinc-lead-copper-silver-iron sulphide bulk concentrate(s) produced from Brunswick Mining and Smelting Company's complex ores. These are:

(1) Sherritt-Gordon Pressure Leaching Process (2) which is totally hydrometallurgical, combining Sherritt's acid pressure leach process with custom-designed solution purification and electrowinning steps.

(2) RPC Sulphation Roast Process (3) which is a combination of pyrometallurgical and hydrometallurgical operations employing a sulphation roast, followed by two-stage leach, solution purification and electrowinning of the metals.

(3) Ferric Chloride Leach Process (4) which is hydrometallurgical, employing ferric chloride as a chlorinating agent followed by solution purification and electrowinning of the metals.

(4) CANMET's Dry-Way Chlorination-Oxidation Process (5,6,7,8,9,10, 11) is a combined pyrometallurgical-hydrometallurgical operation consisting of the chlorination of the sulphide concentrate by chlorine gas, pyrometallurgical oxidation of the iron chlorides by chlorine and/or oxygen, followed by aqueous leaching, solution purification and electrowinning.

Over the long term the chlorination concept appears to be attractive since the pyrometallurgical reactions are autogenous and elemental sulphur can be produced, thereby eliminating the environmental problems associated with pyrite disposal and SO_2/acid rain formation. Furthermore, the chlorine must be recovered for recycling to the extraction steps where the efficiency and recovery of valuable components from the concentrate is high.

Initially the emphasis at CANMET's laboratories had been on the development of low temperature (350°C maximum) chlorination (5,6,10) employing a self-cleaning twin-screw reactor. Expanded interest was subsequently directed toward the development of higher temperature processes (>500°C) (9,19) which produce a molten chloride product. Also, alternate modes of chlorination are being studied, such as a solid-sulphide/Cl_2-gas burner (12) or a vessel having submerged-lance or tuyeres-type chlorine injection.

The principle of utilizing chlorine gas injection, at higher temperatures and under atmospheric pressure, to convert complex metal sulphide concentrates to metal chlorides and sulphur was first patented by J. Swinburne and the process details were presented to the Faraday Society in England in 1903. This process was gradually upscaled and operated during the 1920's, with a maximum eventual thoughput of 420 kg/h. E.A. Ashcroft published a comprehensive process status paper in 1933 (13). Pilot-plant locations were first at Wolverhampton, England (Magnesium Company, Ltd.) and later at Avonmouth, England, operated by the Australian Broken Hill Company ... cooperation with Bewick, Moring and Co. The Wolverhampton pilot plant was scaled at 42 kg per hour. The total process did not gain commercial acceptance since successful development broke down at the step which involved electrolysis of fused zinc chloride. This step was essential to the economic viability of the process. Technology to recover zinc from fused salt and aqueous chloride electrolytes is currently available (14,15).

This report deals with the chemical aspect of metal sulphide-metal chloride-chlorine reactions. Experiments were designed to provide the following:

(1) an understanding of the chemistry, and physical behaviour, of the systems of interest;
(2) an indication of the effect of alkali metal chloride additions to the bath in the chlorination process;

(3) conditions for optimum operation;
(4) methods for collection of metal chloride fume, elemental sulphur and sulphur chlorides;
(5) an indication of suitability of selected materials for construction;
(6) ideas for a conceptual design for the reactor;
(7) mass and energy balances;
(8) confirmation of sample preparation and analytical techniques.

Other vital unit operations in the overall flowsheet, namely, deferrination of the product metal chlorides (6,9), dechlorination of iron chlorides (9) and flash chlorination (12) have been investigated.

THEORETICAL CONSIDERATIONS

During the chlorination of the Brunswick sulphide bulk concentrate (approximate content 30% Zn, 10% Pb, 1% Cu, 20% Fe, 36% S, 0.02% Ag and 3% refractory oxides; detailed composition is given in Tables 1 and 2) the following five chemical reactions can occur:

$$MS_n + \frac{y}{2} Cl_2 \rightarrow MCl_y + \frac{n'}{m} S_m + \frac{n''}{p} S_p + \frac{n'''}{q} S_q + \text{---} \qquad (1)$$

where n and y are the numbers of gram-atoms of sulphur and chlorine respectively and where $(n' + n'' + n''' + \text{---}) = n$; m, p and q etc. represent the number of gram-atoms of sulphur in the particular gaseous sulphur species present in the vapour phase at chlorination temperature; M is the metal component (in g-atoms).

$$MS_n + S_xCl_y \rightarrow MCl_y + \frac{n + x}{m} S_m \qquad (2)$$

where x is the number of gram-atoms of sulphur in sulphur chloride. The temperature dependent sulphur specie distribution would parallel the expansion indicated in Eq (1).

Table 1 - Brunswick bulk concentrate head assay

Element	Wt %	Element	Wt %
Zn	30.23 (29.9)(1)	Ba	0.01
Fe	20.50 (19.9)	Te	<0.005
Pb	10.10 (9.5)	Se	<0.002
Cu	0.65 (0.7)	Be	<0.001
S	37.33 (36.6)	B	<0.001
Si	0.41	P	<0.01
Ca	0.31	Mo	<0.001
Al	<0.04	W	<0.01
Mg	0.09	Cr	<0.001
As	0.23	Ba	<0.001
Ag	0.026	Nb	<0.001
Sn	0.087	Ta	<0.01
Sb	0.069	Ge	<0.001
Cd	0.060	V	<0.001
Mn	0.05	Li	<0.01
Bi	0.014	In	<0.001
Co	0.015	Zr	<0.001
Ni	0.003	Ti	<0.001
C	0.30	Na	<0.001
O_2	2.07	Sr	<0.01
$SO_4^=$	1.3	Pt	<0.2 ppm
Hg	0.0011	Pd	<0.1 ppm

(1) Normal variation in feed

Table 2 - Mineral composition (17) of Brunswick concentrate

Mineral		Wt %
sphalerite	ZnS	49.38
pyrite	FeS_2	32.88
galena	PbS	9.37
chalcopyrite	$CuFeS_2$	1.86
tetrahedrite	$(Cu,Ag,Zn,Fe,Hg)_{12}\pm(Sb,As)_4\pm S_{13}$	0.25
stannite	Cu_2 Fe Sn S_4	0.21
arsenopyrite	FeAsS	0.46
bouronite	$PbCuSbS_3$	<0.01
meneghenite	$Pb_{13}CuSb_7S_{24}$	<0.01
pyrrhotite	FeS	0.01
magnetite	Fe_3O_4	0.01
cassiterite	SnO_2	0.04
dolomite	$MgCO_3$	0.38
calcite	$CaCO_3$	0.54
siderite	$FeCO_3$	1.80
cerussite	$PbCO_3$	0.01
quartz	SiO_2	0.90
anglesite	$PbSO_4$	1.98
excess S		0.27
Total		100.39

$$2FeCl_2 + Cl_2 \rightarrow 2yFeCl_3 + \frac{2-2y}{2} Fe_2Cl_6 \qquad (3)$$

$$\frac{x}{m} S_m + \frac{y}{2} Cl_2 \rightarrow S_xCl_y \qquad (4)$$

As shown below, the ferric chloride can also serve as a chlorinating agent

$$MS_n + Fe_yCl_{3y} \rightarrow y\ FeCl_2 + MCl_y + \frac{n}{m} S_m \qquad (5)$$

where y = 1 and/or 2 and $\frac{n}{m}$, again, represents sulphur specie distribution as shown for reaction (1).

FREE ENERGIES OF CHLORINATION

Figure 1 depicts the standard free energies of reactions of interest as a function of temperature with the sulphur specie being taken as S_2. Calculations were obtained by using the F.A.C.T. (Facility for Analysis of Chemical Thermodynamics) system (15). The absolute standard free energies are thus only valid at the higher temperatures (~650°C) where the S_2 specie predominates (see Fig. 2). Taking into account variable sulphur species as would be the case at lower temperatures, the $\Delta G°$ for chlorination would become more negative than shown in the diagram. For example, in the case of PbS + Cl_2 at 300°C $\Delta G°$ = -43.4 kcal/mole and ZnS + Cl_2 at 300°C $\Delta G°$ = -31.9 kcal/mole as compared to -39.0 kcal/mole and -27.2 kcal/mole respectively. The aforementioned calculation base was employed to obtain these values. As shown in Fig. 1, all of the metal sulphides in the concentrate will chlorinate, with the PbS + Cl_2 reaction having the highest negative standard free energy. This implies that if sulphides other than PbS are chlorinated prior to the PbS then these chlorides, given contact, will serve as chloride donors and back react according to:

$$\frac{2}{y} MCl_y + PbS \rightarrow PbCl_2 + M_{2/y}S \qquad (6)$$

Based on calculations, sulphur chlorides can form according to reaction (4) and they, in turn, can act as chlorinating agents. The standard free energy of formation of S_xCl_y becomes less negative with increasing temperature. Because $FeCl_3$ will also serve as a chlorinating agent and reduce to $FeCl_2$ in the presence of metal sulphides, only a limited amount of $FeCl_3$ should form in the bath if metal sulphides are present. As a result, the formation of $FeCl_3$ can be controlled, at the higher temperature, if the quantity of reactant chlorine added is controlled. Ashcroft (13) stated that the initial evolution of S_xCl_y (at 600°C, while chlorinating a sulphide concentrate similar to the New Brunswick bulk concentrate) indicated that the desired conversion of the metal sulphides to metal chlorides was complete and that the preferred stoichiometry was satisfied. Further chlorine addition would yield

FIG 1 STANDARD FREE ENERGIES OF REACTION AS A FUNCTION OF TEMPERATURE

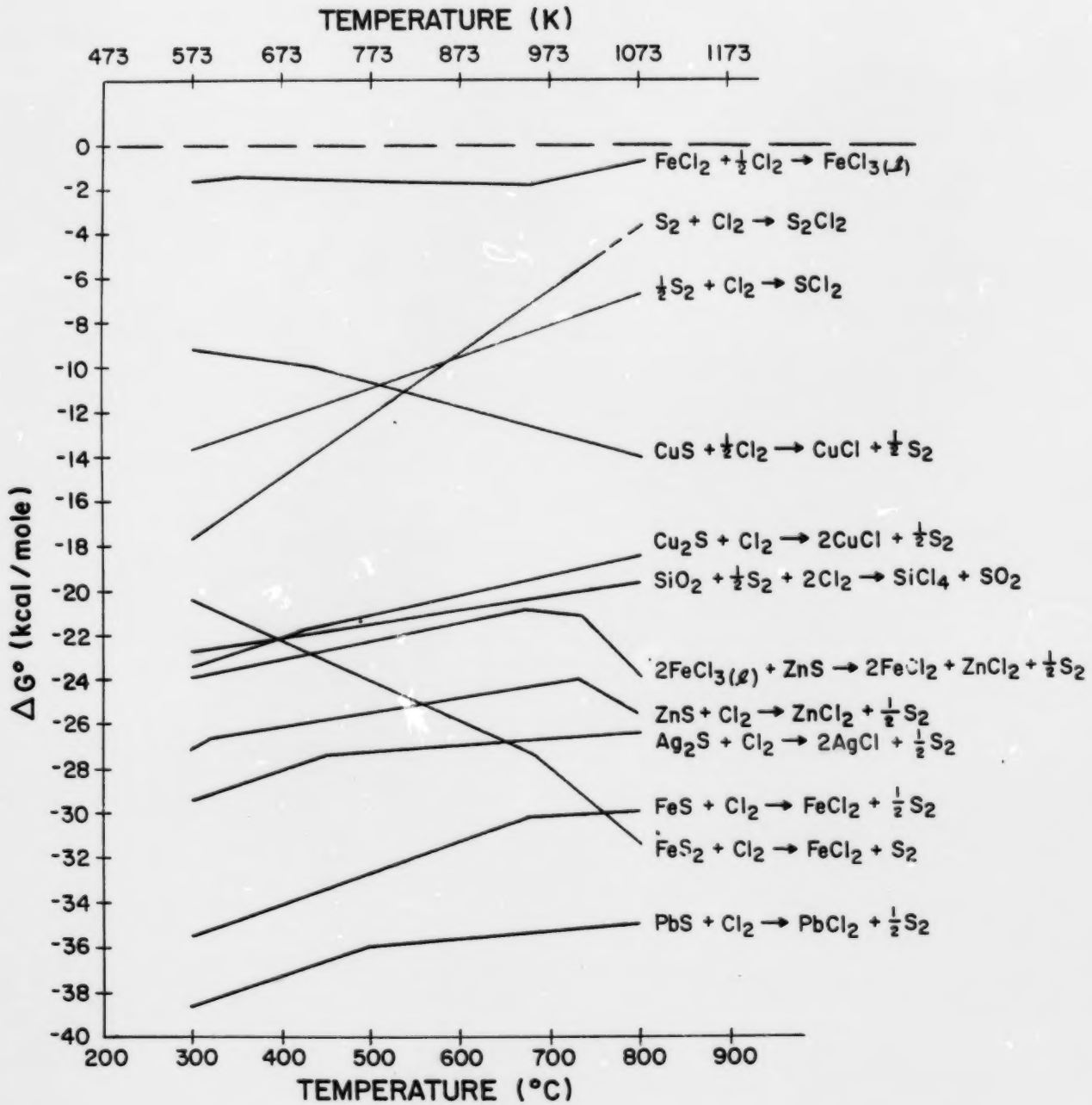
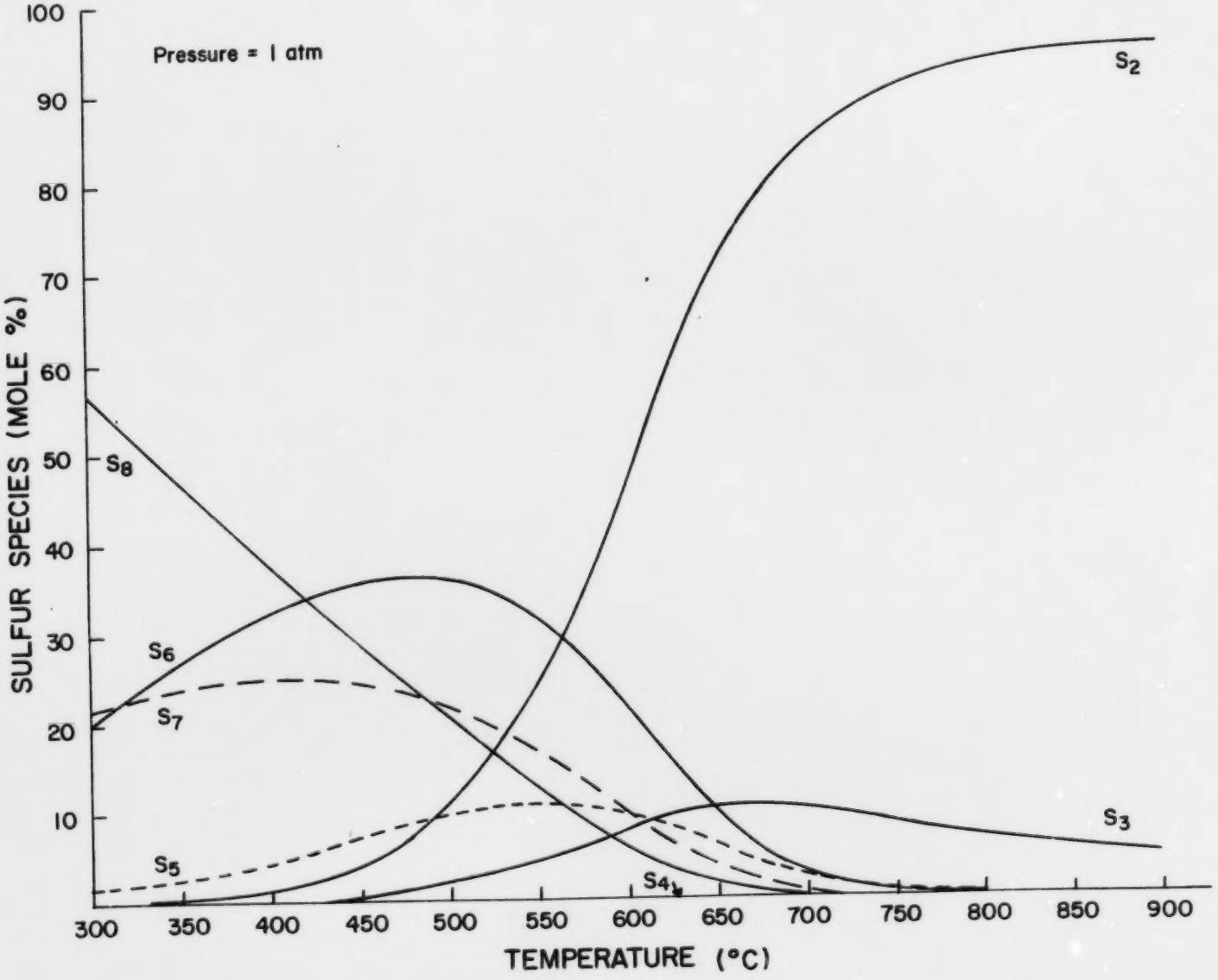


FIG 2 MOLE % SULPHUR SPECIES IN GAS PHASE AS A FUNCTION OF TEMPERATURE



copious fuming of ferric chloride. From a kinetic viewpoint, it has not been established that the interaction of ferric chloride with MS_n is more rapid than the fuming of ferric chloride from the bath when chlorination at temperatures >600°C is pursued.

Since the environment during chlorination is composed, in part, of sulphur (a reductant) and chlorine (an oxidant) some of the gangue materials (e.g., SiO_2) will also react as is evident from the standard free energies of reaction (Fig. 1). This type of reaction could be a limited source of SO_2 in the process.

VAPOUR PRESSURES OF METAL CHLORIDES AND SULPHUR

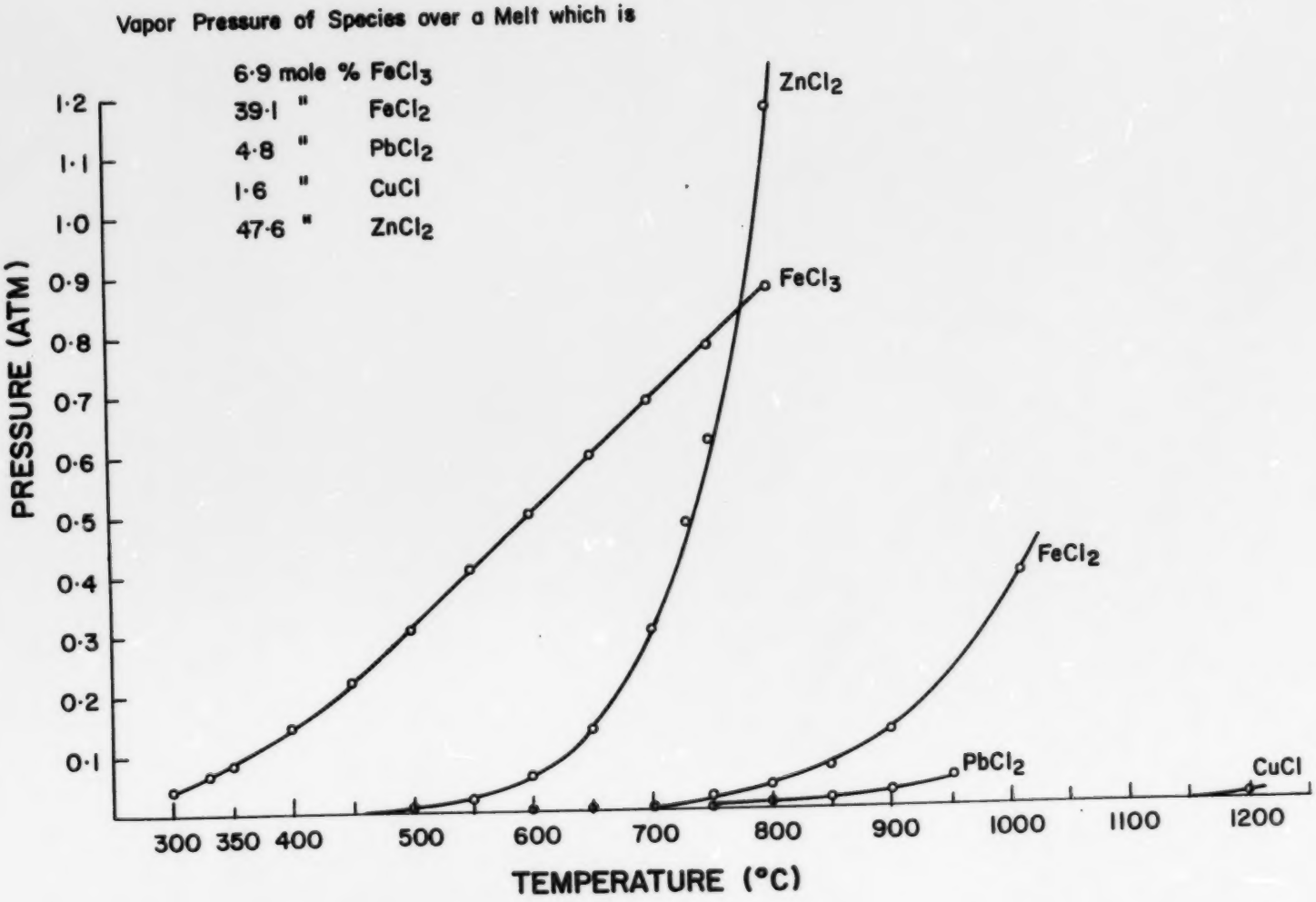
The vapour pressures of metal chlorides over the totally chlorinated bath to which a slight excess of chlorine has been added and which consists of: 47.6 $ZnCl_2$, 39.1 $FeCl_2$, 6.9 $FeCl_3$, 4.8 $PbCl_2$, 1.6 CuCl (mole %), are given in Fig. 3. The curve for $FeCl_3$ vapour pressure is actually the total pressure due to both $FeCl_3$ and the dimer Fe_2Cl_6. The values were obtained by multiplying the vapour pressure of the chloride over its pure chloride by the mole fraction in the melt, i.e.,

$$P_i = X_i P_i^o$$

where P_i = partial pressure of component i over melt
X_i = mole fraction of component i in melt
P_i^o = pressure of component i over pure i

Thus in the case of zinc chloride, for example, at 700°C its vapour pressure is 0.63 atmosphere over a pure $ZnCl_2$ melt, but only 0.3 atmosphere above the molten bath. Even with the substantially lower concentration of $FeCl_3$ in the final melt, its vapour pressure is higher than that of $ZnCl_2$ up to about 775°C. This fact was used to develop a step for deferrination of the bath by chlorination during the next phase of an overall process. If any sulphides are present, the zinc chloride will have the highest vapour pressure since the $FeCl_3$ concentration will be lowered due to its tendency to serve as a chlorinating agent.

FIG 3 VAPOUR PRESSURE OF SPECIES OVER MELT



Alkali metal chlorides are added to metal chlorides to lower their activity and hence their vapour pressures. The effect is significant when "clusters" or complexes are formed with the alkali metal chloride. For example, the vapour pressure of $ZrCl_4$ at 334°C is 1 atmosphere. By fusing the compound CsCl with $ZrCl_4$ the vapour pressure of $ZrCl_4$ is lowered substantially to 1 x 10^{-10} atmosphere at 340°C (X_{ZrCl_4} = 0.1) (16). Assuming an ideal solution, the dilution due to CsCl should have lowered the vapour pressure of the $ZrCl_4$ to only 0.1 atmosphere at 340°C. For the melts under consideration in this report, some lowering of vapour pressures of the metal chlorides is expected when alkali metal chlorides are added. However, this is primarily due to a dilution effect since no strong complex compounds of these base metal chlorides with alkali metal chlorides have been identified.

Figure 2 shows the equilibrium composition of the various sulphur species in the gas phase as a function of temperature. In the domain of low temperature chlorination (~300°C) the total sulphur pressure over elemental sulphur is only 0.07 atmosphere, with the predominant species being S_8, S_6 and S_7. Negligible S_2 exists at this temperature. At higher temperatures (675°C), the sulphur vapour pressure is 9.1 atmospheres with 80 mole % of the gas phase being S_2 and 10 mole % being S_3. It is important to take into account the distribution of sulphur species when calculating the thermodynamic properties of the system and for computation of off-gas volumes when considering scaled-up reactor design.

ENTHALPY CALCULATIONS

For the enthalpy calculations the thermodynamic properties of the binary sulphide compounds (MS_n) were used. In the real system, however, chalcopyrite and other more complex minerals will exist (Table 2). Thermodynamic data are lacking for these complex minerals and they can be non-stoichiometric. However, since the predominant minerals (17) are sphalerite, pyrite and galena (total = 92%) and since no other major elements were neglected (e.g., Cu), the error introduced by neglecting the others would be small.

The adiabatic flame temperature (where $\Delta H = 0$) was calculated by using the F.A.C.T. system (18). For the adiabatic reaction between the metal sulphides and gaseous chlorine, both initially at 25°C, producing metal chlorides and S_2 vapour only, the flame temperature is 768°C. However, when the

vapour was considered to be a mixture of sulphur species, as dictated by the gaseous equilibrium (Fig. 2), then the calculated adiabatic flame temperature became 790°C. In order to perform this calculation, an iterative procedure was used. The equilibrium sulphur species were first established at a selected temperature. These species and their concentrations, together with the temperature, were then used to calculate the heat of reaction. This procedure was repeated until $\Delta H = 0$.

If excess chlorine is added to the system some of the $FeCl_2$ will be chlorinated to $FeCl_3$ and the flame temperature will again increase. For example, at equilibrium, with 5% excess chlorine and the existing sulphur species, the temperature will rise to 810°C.

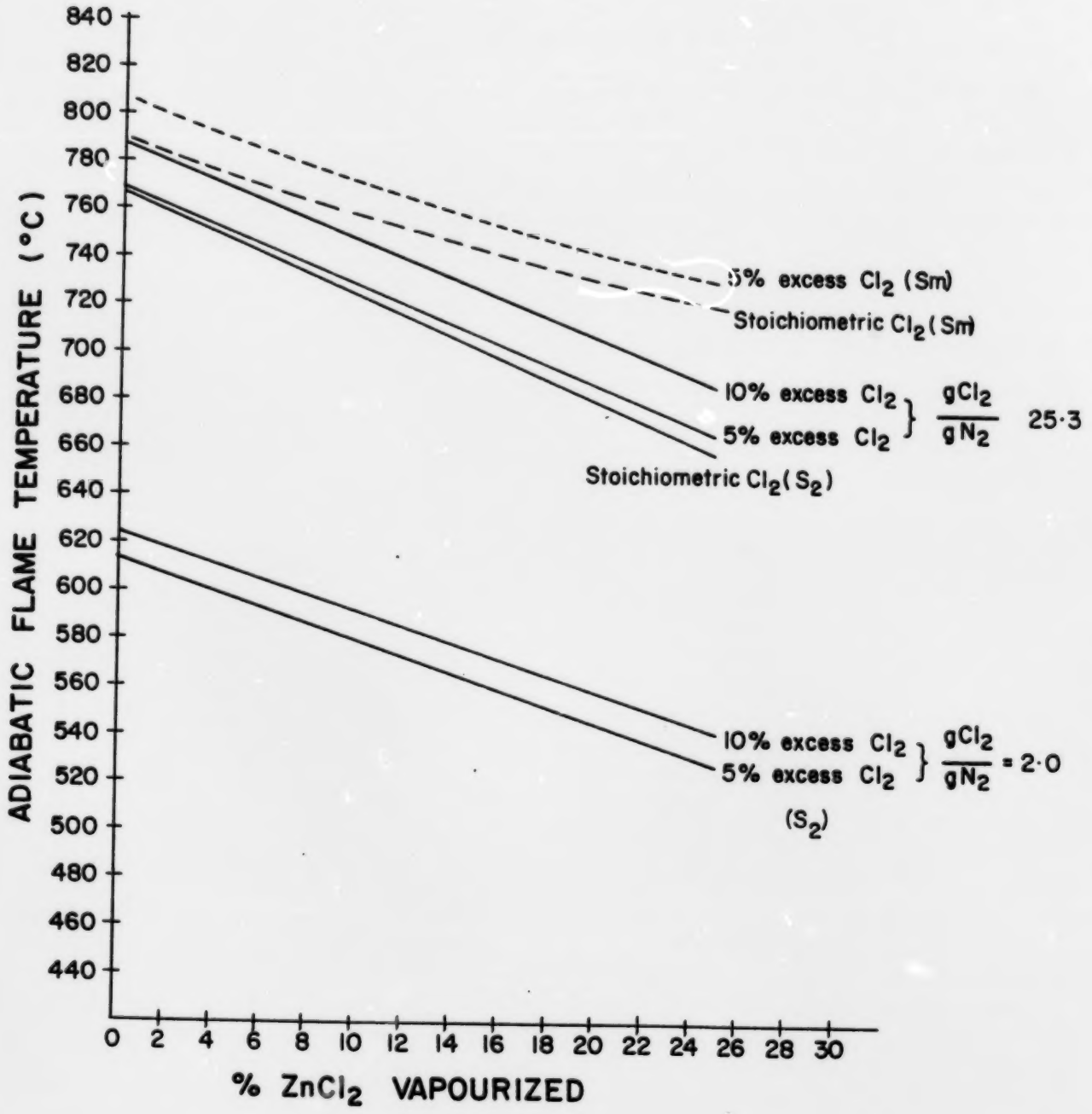
In the real system, fuming of metal chlorides will take place with $ZnCl_2$ being the primary vapour specie when the liquid $FeCl_3$ concentration is low (<~15 wt/%). Ferric chloride species (Fe_yCl_{3y}) will fume if the chlorine input is not carefully controlled. A family of curves showing the effect of various levels of fuming on the adiabatic flame temperature can be seen in Fig. 4. For example, if 10% of the zinc chloride fumed, the adiabatic flame temperature would drop from 790°C to 760°C (stoichiometric chlorine and S_m).

In the commercial process it may be advantageous to use a nitrogen carrier gas for sulphur and for agitation of the bath if an above-the-melt Cl_2/MS_n burner is used. The effect on the flame temperature of adding various quantities of nitrogen gas to the chlorine is also illustrated in Fig. 4.

PHASE DIAGRAMS

The F.A.C.T. system developed at McGill University and Ecole Polytechnique (18,19,20) was utilized to generate the phase diagrams of interest for the system. The ternary phase diagrams showing the liquidus isotherms for the $ZnCl_2$-$PbCl_2$-$FeCl_2$ and $ZnCl_2$-$PbCl_2$-$FeCl_3$ systems are shown in Fig. 5 and 6 respectively (composition scales are in mole per cent and the numbers are temperatures in degrees Celcius). No information was available in the literature on the $FeCl_2$-$FeCl_3$ binary phase diagram and hence the F.A.C.T. system could not be used to calculate the quaternary $ZnCl_2$-$PbCl_2$-$FeCl_2$-$FeCl_3$ system. CuCl was not considered as a necessary component in the liquidus isotherms calculation since its concentration is relatively low and it is not expected to significantly affect the liquidus temperature.

FIG. 4 ADIABATIC REACTION TEMPERATURE AS A FUNCTION OF $ZnCl_2$ FUMED UNDER VARIOUS CONDITIONS



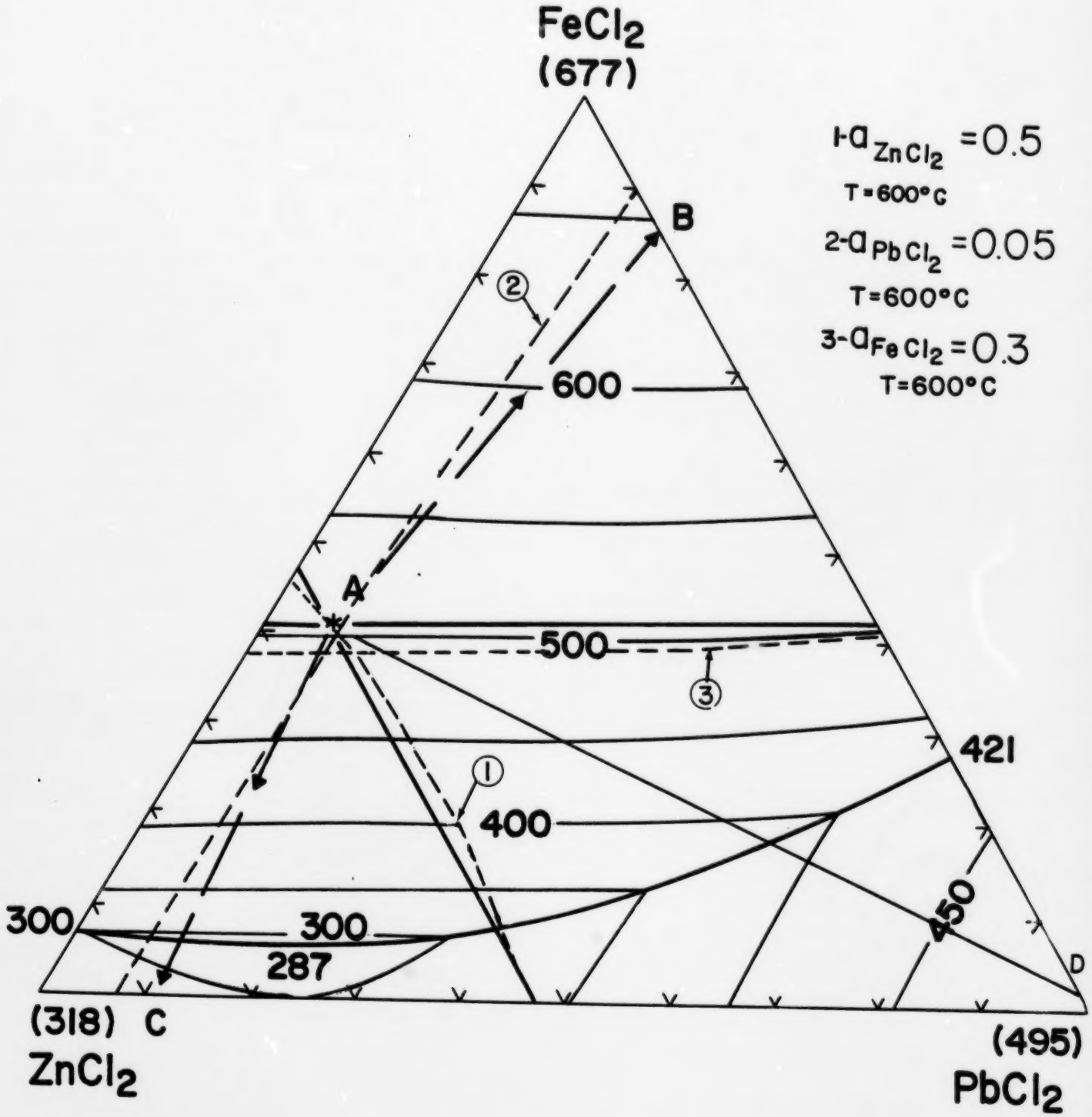
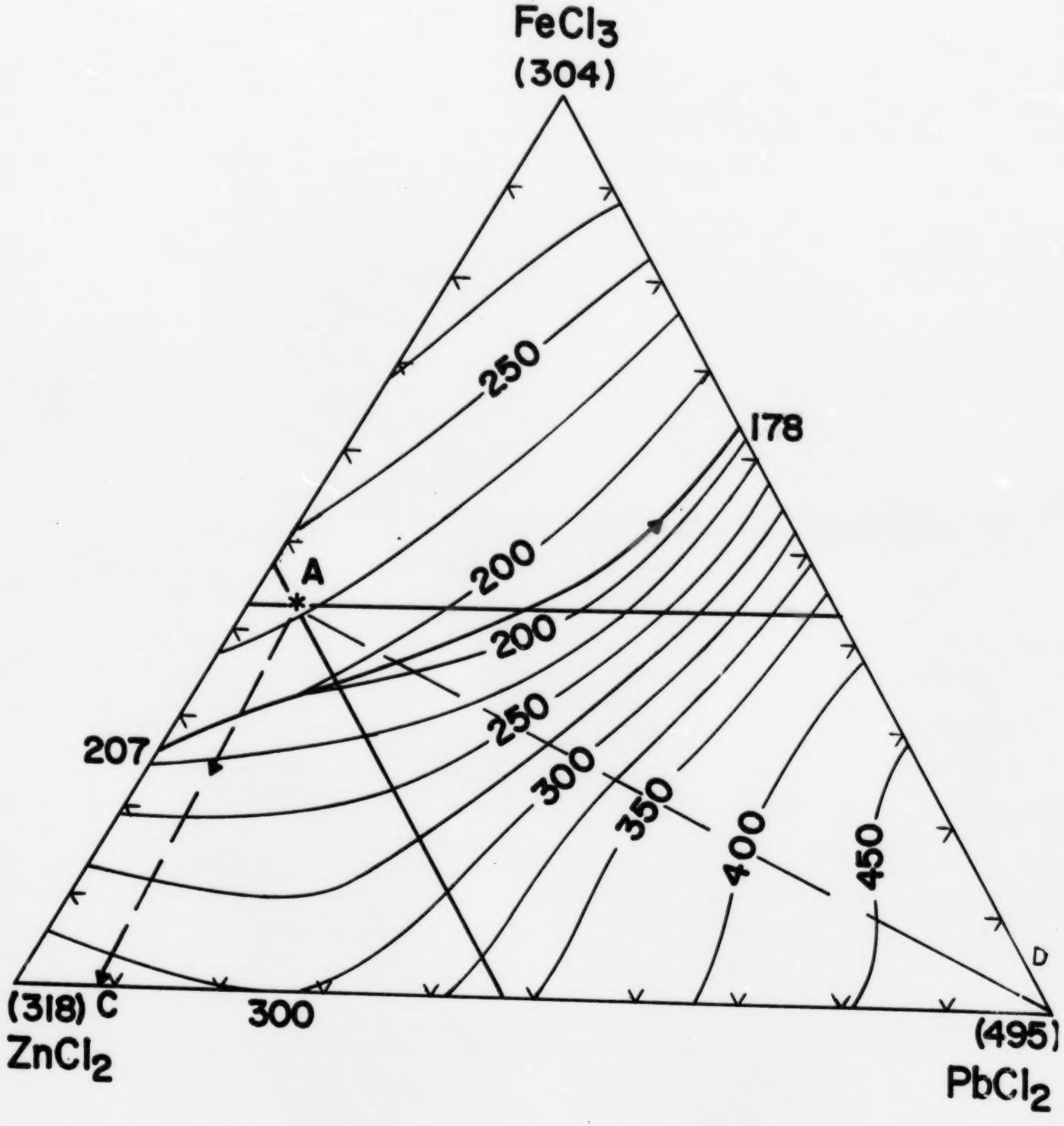


FIG 5 TERNARY PHASE DIAGRAM FOR THE $ZnCl_2$ - $PbCl_2$ - $FeCl_2$ SYSTEM SHOWING SELECTED ISOACTIVITY LINES.

CONCENTRATION IN MOLE %.

FIG 6 TERNARY PHASE DIAGRAM FOR THE $ZnCl_2$ - $PbCl_2$ - $FeCl_3$ SYSTEM
CONCENTRATION IN MOLE %



Based on the two ternary phase diagrams shown in Fig. 5 and 6, on which are superimposed the expected melt compositions which agree with those found experimentally, it is possible to estimate the melting temperature of the bath. Also superimposed are the iso-activity lines which confirm that the solutions are close to ideal mixtures. Assuming 15% $FeCl_3$ in the fully chlorinated bath (typical experimental result) the predicted melting temperature is 460°C. The liquidus points of chlorinated products of composition similar to point A were determined using the differential thermal analysis technique (DTA) and were found to range between 400°C and 500°C. Limited fuming of ferric chloride is observed under these conditions. As is obvious from the ternary phase diagram the quantity of $FeCl_3$ in the mixture has a significant effect on the melting point. Referring to Fig. 5, as $ZnCl_2$ fumes the melting temperature moves along line A-B. The temperature traverses A-C as $FeCl_2$ is chlorinated and the ferric chloride fumes off (refer to Fig. 6). Both $ZnCl_2$ and Fe_yCl_{3y} may fume at a rate which maintains the ratio of $ZnCl_2/FeCl_3$ in the bath. In this case the melting points would move along the line A-D. If the fuming rates differ, then a family of curves (m.p.) would result (i.e., C → D → B). It is significant that, for the postulated concept of iron removal by converting $FeCl_2$ to Fe_yCl_{3y}, the bath can be operated at a lower temperature. In this deferrination step the desired operating temperature may be less than 500°C.

The effect of NaCl addition on the melting temperature of the chloride mixture is illustrated in Fig. 7. With 10 wt % NaCl in the bath (indicated by composition at *) the melting temperature is expected to be approximately 425°C. This lowering of temperature in chloride systems to which alkali metal chlorides have been added is a relatively common occurrence in MCl_y-NaCl systems.

LABORATORY BENCH SCALE TESTS

Properties of Sulphide Concentrate Feed

The chemical composition of the Brunswick bulk concentrate is given in Table 1. The major elements monitored during the experimental program were Zn, Fe, Pb, Cu, Ag, S and to a lesser degree As. Two sets of analysis (using the same methods) for the main elements appear in the table and reflect a typical variation in composition of the concentrate. The gangue content of

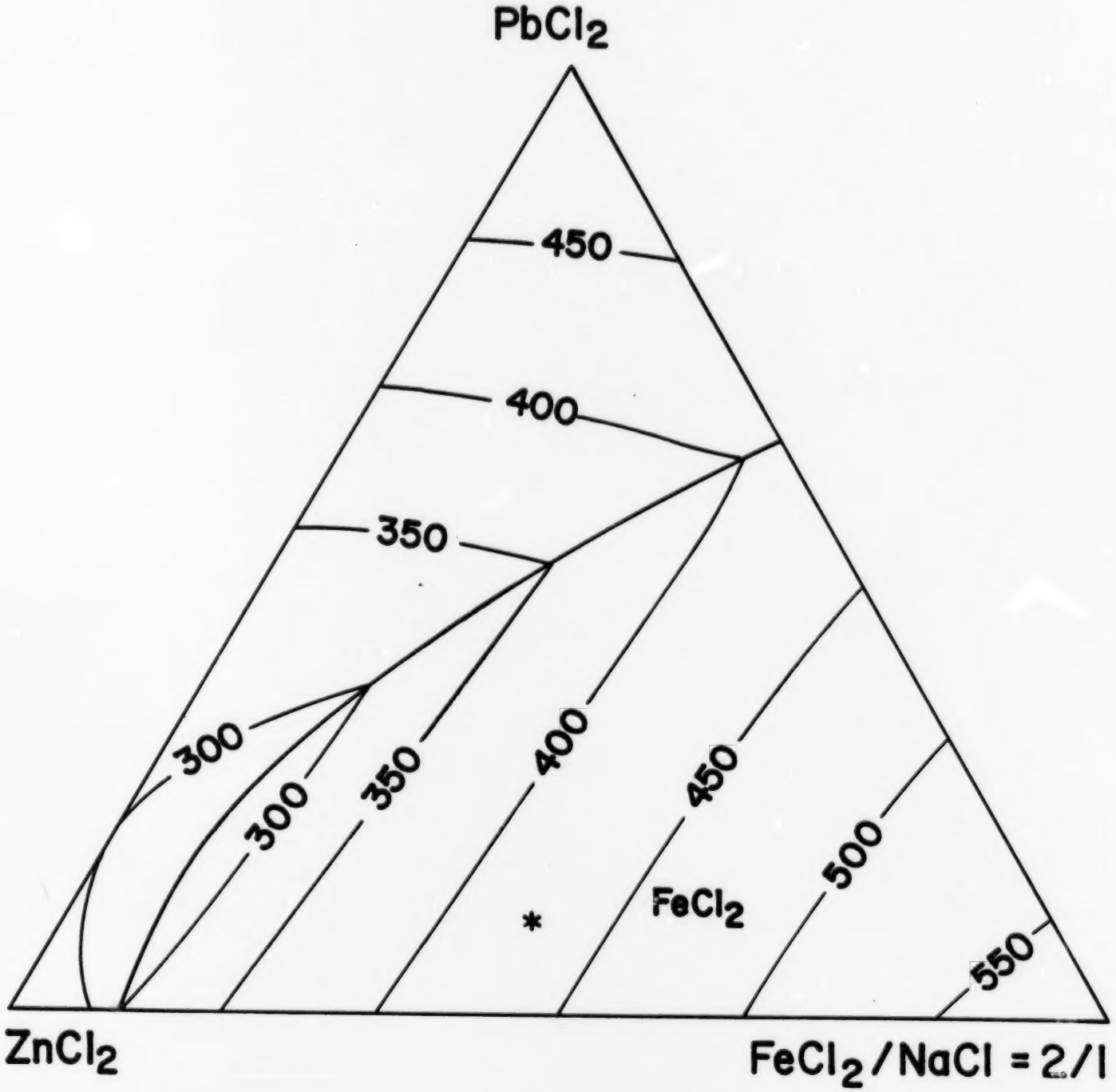


FIG 7 SECTION FROM QUATERNARY PHASE DIAGRAM FOR $PbCl_2$ - $ZnCl_2$ - $FeCl_2$ - NaCl SYSTEM. $FeCl_2$/NaCl=2/1 CONCENTRATION IN MOLE %.

the concentrate is approximately 3% and is comprised primarily of SiO_2, CaO, MgO and C. Some of the carbonaceous component would have come from the flotation circuit.

The water-insoluble sulphate component is primarily lead sulphate which probably formed as a result of oxidation of galena during storage of the sample. However, the dried, as received concentrate also contained a water-soluble fraction equal to 3.3% of the concentrate weight. Upon analysis, the white "salt" was shown to consist of the following components,

$ZnSO_4$	64%
$CaSO_4.2H_2O$	31%
Na_2SO_4	4%

The source of the $ZnSO_4$ and gypsum is not obvious. Solid-liquid separation of the bulk flotation product was reported to have been difficult.

Additional elements which could be of concern in the processing circuit and which should eventually be monitored are As, Cd, Bi, Sb, Co and Ni.

The mineralogy (17) of the bulk concentrate is summarized in Table 2. The highest concentration minerals are sphalerite, pyrite, galena and chalcopyrite. For calculation purposes (mass balances, heat balances, free energy determinations, chlorine balances) only the following sulphides were considered: ZnS, PbS, Cu_2S, FeS, FeS_2, Ag_2S. The method for calculating the quantity of FeS and FeS_2 is given in Appendix 1. The assumptions involved herein are expected to yield a very close approximation to the actual situation. The proportion of chalcopyrite in the concentrate is relatively small. Cu_2S was selected as the copper sulphide specie present since it is thermodynamically more stable than CuS.

The size distribution of the sulphide concentrate is given in Table 3. Approximately 80% of the material is minus 325 mesh. This fine grind is necessary to obtain higher metal recoveries in the beneficiation process (>95%). The finely divided material would be advantageous if a Cl_2/sulphide burner is used for chlorination. For submerged-lance chlorination on an industrial scale the feed may have to be pelletized to minimize dusting.

The specific gravity of the concentrate is 4.64.

Table 3 - Size distribution of concentrate

Mesh	Wt %
+100	0.8
-100 + 200	2.3
-200 + 270	8.5
-270 + 325	9.7
-325 + 400	5.0
- 400	73.8

Apparatus and Experimental Procedures

(i) Feed and reagents

The sulphide concentrate, described in the previous section, was dried either under nitrogen or air at approximately 90°C for at least 48 h. No significant increase of sulphate content was observed after drying in air. The dried concentrate was stored in sealed containers until required.

Reagent grade sodium chloride was dried for at least 24 h in air at 100°C and stored in sealed containers.

The chlorine and nitrogen gases used throughout the experiments were of high purity and were dry. To determine chlorine consumption and material balances, 0.5 kg and 2.3 kg chlorine bottles were employed and were continuously weighed during the experiments.

All chemicals used for sample preparation and analysis were analytical grade.

(ii) Apparatus

Figure 8 shows the bench-scale batch chlorination assembly. The temperature profiles for two typical batch-type experiments are given in Table 4. The chlorination vessel was constructed from Vycor glass tubing, which was approximately 25-30 mm in diameter and 75 cm long. The weight of feed was usually 125-200 g, and when chlorinated, yielded a chloride product of 9 to 16 cm in length after solidification. At no time was the bath depth less than 11 cm. The product weight was 1.2 to 1.25 times the weight of concentrate feed. The expansion of solid product to a liquid bath, upon heating

FIG 8 HIGH TEMPERATURE BENCH SCALE BATCH CHLORINATION ASSEMBLY

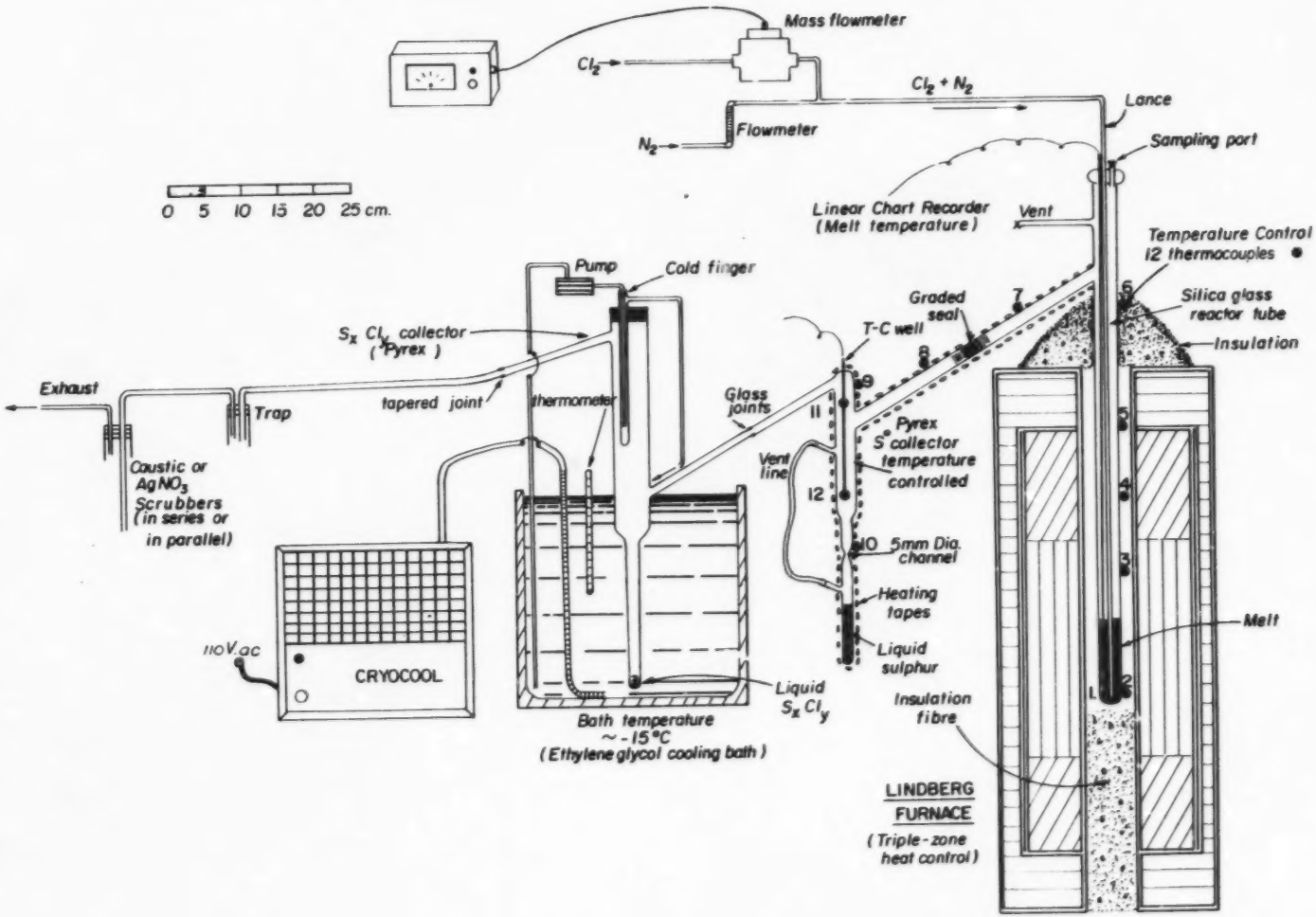


Table 4 - Typical temperature profile in experimental circuit (1)

Thermocouple number	Test conditions 500 °C	725°C
1(2)	506	722
2	501	708
3	496	695
4	480	668
5	442	622
6(3)	313	355
7	330 - 380	
8	200 - 225	
9	180 - 210	
10	180 - 220	
11	160 - 200	
12	140 - 170	

(1) Refer to Fig. 8 for thermocouple location.

(2) Internal temperature.

(3) No. 6 temperature drop was due to cooling from the reactor head which received limited heat input and could not be heavily insulated. However, no noticeable problem resulted. This region remained "clean".

to reaction temperature, was the order of 30%. A ground-glass fitting was utilized for the reactor top. It included ports for a lance to inject Cl_2 plus N_2, for a thermocouple well and for sampling purposes. Vapours were exhausted via a Vycor side arm. The chlorinator was heated in a 6.3 cm I.D. Lindberg split-half furnace (vertical, electrical resistance type with on-off control). A graded Vycor-Pyrex seal joined the reactor to the sulphur collector. The use of additional insulation above the furnace, and wound heaters on the side arm, ensured that sulphur would readily transfer from the upper part of the reactor to the sulphur condenser. The side arm was maintained at approximately 400°C to minimize sulphur deposition. When the split-half

furnace was momentarily, and slightly opened, vapours could be seen refluxing above the bath, with the liquid draining down the walls. The sulphur collector was wrapped with heating tapes to maintain the internal temperature at 150°C. This ensured that the condensed liquid sulphur was approximately at its minimum viscosity. The relatively pure sulphur gas condensed on the walls of the collector and flowed freely downward through the 5 mm channel into the lower chamber, thus reducing contact between the sulphur and any free chlorine. In this manner the formation of sulphur chlorides was minimized.

The off-gases from the sulphur collector passed to a Pyrex sulphur chloride condenser. A "Cryocool" refrigeration unit was used to maintain the condenser's cooling liquid at -10 to -15°C.

Exhaust gases from the sulphur chloride condenser, containing unutilized Cl_2, uncondensed S_xCl_y and S_m, a trace of metal chlorides and probably a small amount of SO_x and CO_x, passed into a scrubber containing 5 M NaOH. Occasionally, $AgNO_3$ solutions were used for scrubbing the Cl_2 in order to determine the instantaneous chlorine utilization efficiency. The liquid levels in the two bubblers were maintained at approximately 3 cm total. No detectable reactive gas exhausted past the scrubbers. This determination was based upon the precipitation of insoluble AgCl, which was filtered off, dried and weighed. However simple this procedure appears, it must be viewed with caution. The condenser off-gas contains small amounts of reducing agents (e.g., SO_2, as well as uncondensed sulphur). As a result, some metallic silver is formed which reports to the precipitate, and therefore analysis of the precipitate becomes a necessity and the main advantage of the procedure is lost.

The gas-containing lines in the circuit were made primarily of Pyrex glass tubing. The connecting links and seals were either of Neoprene rubber tubing, or tapered or ball-type ground joints. Silicone grease or Halpen 726 cement was used on the joints.

Volumes of gases entering the system were measured by either mass or rotameter type flowmeters.

Temperatures were measured with liquid thermometers, chromel-alumel thermocouples and platinum-platinum/10% rhodium thermocouples. The output from the thermocouples was displayed on a printer, a strip chart recorder or a digital meter. The locations of the thermocouples are shown in Fig. 8 with the corresponding temperatures given in Table 4.

(iii) Chlorination

The calculated chlorination mass balance is summarized in Table 5 showing that approximately 0.6 grams of chlorine (stoichiometric) are required per gram of concentrate. The weight of chlorinated product is 1.2 grams and 0.4 grams of sulphur are produced. Stoichiometric chlorine is defined as the quantity of chlorine required to produce the non-ferrous metal chlorides, elemental sulphur and ferrous chloride. Ferrous chloride is the desired iron compound formed during the chlorination step. Ferric chloride formation will result in some contamination of the sulphur due to the relatively high vapour pressure of this iron compound.

The solid, dried concentrate, NaCl and/or chlorinated starter "heel" were poured into the Vycor reactor through a long-tube funnel. This funnel minimized dust deposition on the walls of the reactor. The chlorine lance and thermocouple well assembly were inserted into the finely divided charge while the reactor was in the horizontal position. A low flow (~20 cm^3/min) of nitrogen was maintained through the lance to prevent blockage of this tube by the charge. The assembly was completed as described previously (Fig. 8). The reactor and off-gas line heaters were turned on. The power input to the off-gas line heaters was controlled by variable voltage transformers. When the temperature of the charge reached 450°C, chlorine and nitrogen were introduced through the lance. The chlorine lecture bottles were preweighed. Approximately 10% by volume N_2 was used as a carrier gas. The temperature of the bath was rapidly raised to the desired level. The usual injection rate of chlorine during the bench scale batch tests was 75 cm^3/min. Due to the relatively low bath depth and the non-optimized design of the injection lance, the chlorine utilization efficiency dropped at higher flow rates. At the completion of chlorination, the system was purged with nitrogen and the melt was solidified under this gas. The end-point of the chlorination was very obvious since at that point, at the higher temperatures of chlorination under investigation, S_xCl_y would begin to evolve and condense in the off-gas assembly. The reactor and contents were allowed to cool naturally by shutting down the heat input. This cooling period was usually overnight. The melt showed obvious segregation but this fact was of no practical consequence. The reactor and ancillary components were broken open as necessary to recover the chlorinated product and all condensed material. Every product was crushed, blended and weighed in a glove bag or dry environment box filled with dry nitrogen or argon to minimize hydrolysis. Selected samples were analyzed.

Table 5 - Calculated chlorination mass balance (basis 100 g concentrate)

Compound	Gram-moles	Weight (g)	Weight Cl_2 requ'd (g)	% of total Cl_2	Metal chlorides weight (g)	% of total metal chlorides	Weight of sulphur evolved (g)	% of total sulphur
ZnS	0.457	44.53	32.4	52.9	$ZnCl_2$ 62.3	51.3	14.7	40.2
PbS	0.046	11.01	3.2	5.2	$PbCl_2$ 12.8	10.5	1.5	4.1
Cu_2S	0.006	0.88	0.4	0.7	CuCl 1.2	1.0	0.2	0.5
FeS	0.083	7.27	5.9	9.6	$FeCl_2$ 10.5	8.6	2.7	7.4
FeS_2 (1)	0.273	32.83	19.4	31.6	$FeCl_2$ 34.6	28.5	17.5	47.8
Ag_2S	0.0001	0.03	<0.01	<0.01	AgCl 0.03	0.02	<0.01	<0.03
		96.6	61.3		121.4		36.6	

(1) Some thermal decomposition also expected

When a starter "heel", NaCl or both were required, the ground materials were blended prior to pouring them into the reactor. The ratio of "heel" to concentrate was usually 3/1. With a "heel", higher chlorine utilization efficiencies were realized due to the rapid formation of a fluid bath when operating temperature (~450°C) was reached. With NaCl (m.p. = 801°C) a bath was also formed due to the interaction of the salt with metal chlorides to result in a lower melting mixture.

(iv) Sample preparation

The following procedure was established for the preparation of the metal chloride samples for chemical analysis.

Approximately 2 grams of the weighed sample was dissolved in 300 mL of distilled water at approximately 50°C. The sample was stirred for 15 minutes at constant temperature and then rapidly filtered through a fritted porcelain crucible. The residue was washed with 50 mL of hot water. Concentrated HCl (100 mL) was added to the filtrate and the solution was made up to 500 mL at 25°C in a volumetric flask. The addition of HCl was essential to stabilize the leach solutions during standing. Without this step, the silver species migrated to, and were absorbed on, the walls of the glass container, thereby leading to significant errors in silver determinations. The low pH also ensured that iron remained in solution. The filtrate was analyzed for the elements of interest by means of the techniques listed below.

The weighed residue, if sufficient in quantity, was recovered from the filter crucible and analyzed. The residue consisted primarily of unreacted sulphides, although a minor gangue component was also present. Table 6 gives the spectrochemical analysis of the gangue materials in the residue which resisted attack by the standardized leach conditions. No explanation can be given at this time as to why the selenium appears to be a major constituent in the residue. A more detailed presentation of the sample preparation techniques can be found in the reports by Bondar-Clegg (21) who conducted the investigation under a CANMET contract.

The leaching of recovered sulphur products was done as follows:

Table 6 - Spectrochemical qualitative analysis of inert residue (1)

Element	Qualitative concentration (2)	Element	Qualitative concentration (2)
Se	1	W	ND
Mg	2	Ga	ND
Al	3	Nb	ND
Pb	3	Ta	ND
Fe	3	Bi	ND
Cu	3	V	ND
Zr	3	Ni	ND
Ag	3	Li	ND
Sn	4	Co	ND
Ca	4	In	ND
Na	4	Ge	ND
Zn	4	Sr	ND
Ti	4		
B	5		
Mn	5		
Cr	5		
Cd	ND		
Ba	ND		
Be	ND		
P	ND		
Sb	ND		
As	ND		
Mo	ND		

(1) Residue after dissolution of sample by the standardized leaching technique as applied to metal chloride product.

(2) 1 = major constituent
2 = minor constituent
3 = strong trace
4 = trace
5 = faint trace
ND = not detected

(1) Approximately 3 grams of weighed, coarse-ground sulphur was thoroughly crushed in a mortar containing a solution of water containing 12 1/2% methanol (V/V) and 1 g NaOH/l. The slurry was transferred to a beaker and digested for 15 minutes at 50°C.

(2) After filtration and water washing with a fritted porcelain crucible, the solution was analyzed for total chloride. This chloride represented the contribution from dissolved chlorine, S_xCl_y or metal chlorides.

(3) A second portion (3 g) of sulphur was crushed in 0.1 M HCl and subsequently leached at 50°C while stirring. The slurry was filtered on a fritted procelain crucible and the sulphur thoroughly water washed. The filtrate was analyzed for zinc, iron and arsenic. The solids were analyzed for sulphur and arsenic.

The analytical techniques which were used for the various elements are summarized below:

Solutions: (leach solution, scrub solution)

Metals (Zn, Pb, Cu, Ag, Fe)	:	by atomic absorption
Anions - SO_4	:	gravimetry
- Cl	:	Volhard method
Fe^{++}/Fe^{+++}	:	titrimetry
As	:	distillation

Solids : (leach residues, feed, sulphur product)

Metals	:	dissolution/atomic absorption
S	:	(1) dissolution of sample/gravimetry if S content high (2) combustion if S content low
Ag	:	usually dissolution/atomic absorption
Fe	:	atomic absorption <u>or</u> titrimetry, after dissolution
As	:	distillation

Results and Discussion

Experimental results are discussed in relation to Fig. 9 through 16 (pp 34-45). Tables 9 to 13 (Appendix 2) show typical material balances. A summary of the tests and the test parameters used is shown in Table 7.

(i) Selection of optimum chlorination temperature

Theoretical calculations showed that the adiabatic flame temperature for the reaction between the metal sulphides in the bulk concentrate and chlorine gas was 790°C. The operating temperature, in a commercial reactor, is expected to be approximately 700°C. This takes into account reasonable heat losses and metal chloride fuming.

The following criteria for selecting the optimum temperature for chlorination of 680°C was based on the theoretical calculations as well as on experimentally-determined requirements.

- maximum recovery of metals as metal chlorides. This implies low residual sulphur in the melt and minimum fuming;
- high chlorine utilization efficiency and relatively rapid rates of reaction;
- minimum formation of S_xCl_y and Fe_yCl_{3y}, and
- fluid melts.

In order to investigate the chemistry of chlorination in fluid melts and to elucidate the effect of temperature on chlorination efficiency, a total of 33 tests were conducted from 500°C to 800°C. The tests were primarily batch type, where the solid sulphide was chlorinated as described previously. Some experiments were carried out with a starter "heel" to which sulphide was added at the beginning and intermittently as chlorination progressed. Chlorination commenced when the starter feed reached the desired reaction temperature. The chlorine and nitrogen gases entering the reactor were at room temperature. However, some preheating of chlorine and nitrogen took place as the gases passed downward through the lance. The results are shown in Fig. 9.

As is apparent from Fig. 9 the maximum recovery of metals, as their chlorides, in the bath is at approximately 660°C. This recovery is the result of maximization of metal sulphide conversion to molten metal chloride while minimizing the volatilization of metal chlorides from the bath. At this

FIG 9 TOTAL METALS RECOVERY AS A FUNCTION OF TEMPERATURE

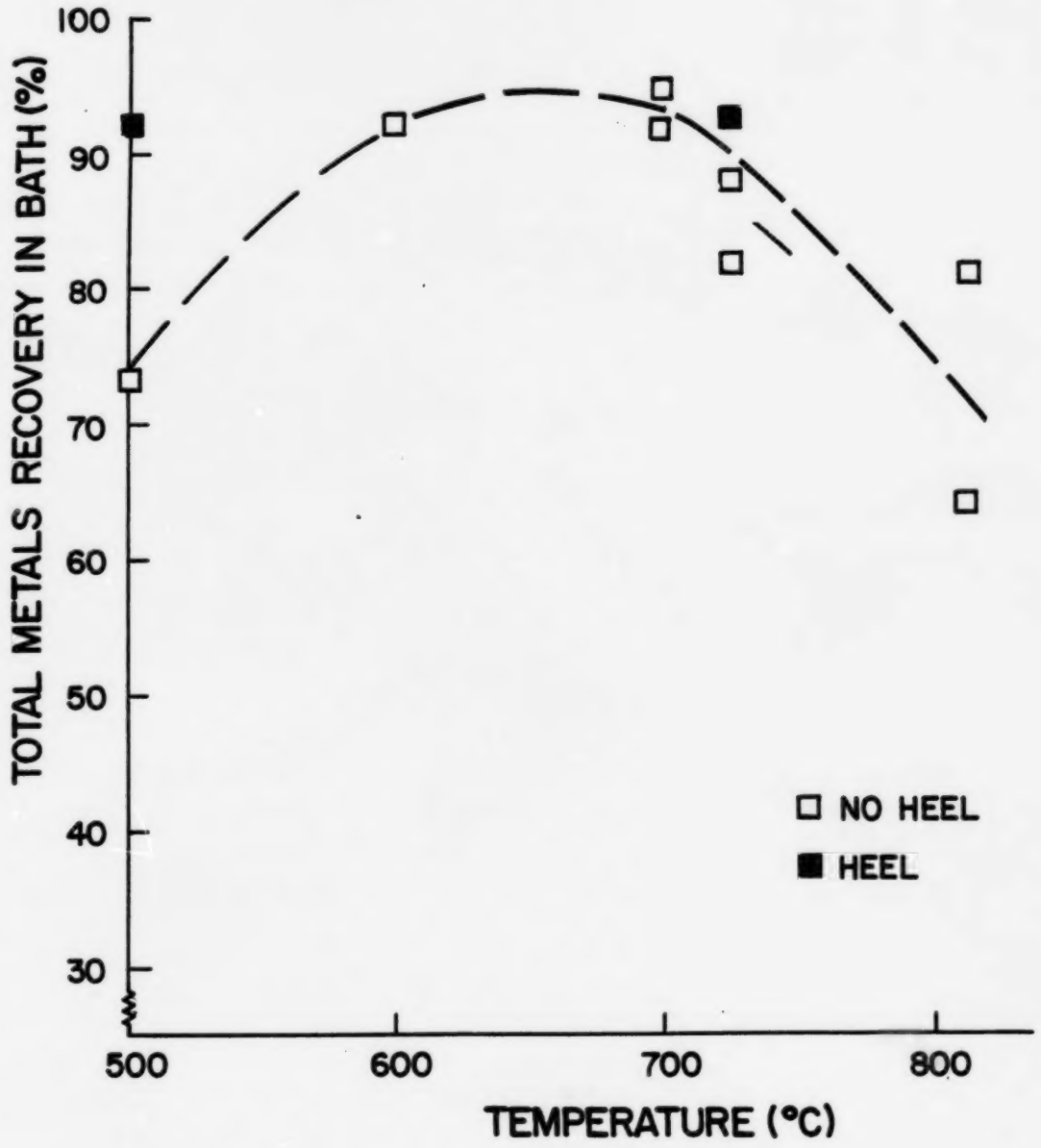


Table 7 - Summary of bench-scale chlorination experiments

Run No.	Charge	Temp °C	Gas flows (cm^3/min) N_2	Gas flows (cm^3/min) Cl_2	Remarks
1	Concentrate	715	10	70	underchlorinated
2	Concentrate	725	10	70	
4	NaCl + Concentrate	700	10	70	conc/NaCl = 5
5	Concentrate	750	10	72	some S_xCl_y excess Cl_2
6	Concentrate	700	10	77	molten NaCl collector for fume
7	Concentrate	580	10	90	some S_xCl_y
8	Concentrate	810	10	90	severe $ZnCl_2$ fuming
9	Concentrate	500	10	74	26% unchlorinated S_xCl_y
10	NaCl + Concentrate	700	10	70	
11	Concentrate	725	10	72	intermittent sampling
12	Heel + Concentrate	725	10	83	
13	Heel + Concentrate	725	10	345	
14	Heel + Concentrate	500	10	80	14% unchlorinated S_xCl_y
15	Concentrate	725	10	150	
16	Concentrate	725	10	300	low Cl_2 efficiency
17	Heel + Concentrate	725	10	77	variable heel/conc ratios: continuous feed

Table 7 (Cont'd)

Run No.	Charge	Temp °C	Gas flows (cm^3/min) N_2	Gas flows (cm^3/min) Cl_2	Remarks	
20	NaCl + Heel + Concentrate	650	10	70	overchlorinated conc/NaCl = 4	
22	Concentrate	650	10	70	Batch size = 450 g leaching experiments deferrination experiments	
24	NaCl + Concentrate	650	10	70	conc/NaCl = 4	
25	Heel + NaCl + Concentrate	650	10	70	conc/NaCl = 4	
26	NaCl + Concentrate	650	10	75	conc/NaCl = 19	
27	NaCl + Concentrate	650	10	75	conc/NaCl = 7	
28	Concentrate	680	10	140		
28B	Concentrate	690	10	140		
29	Concentrate	680	10	250		
30	Concentrate	775	10	75		
SV-1	Concentrate	775	10	74	15% unchlorinated	
SV-2	Concentrate	680	10	75	intermittent sampling	
SV-3	Heel + Concentrate	680	10	75	intermittent sampling	
L-1	NaCl + Concentrate	650	10	135	conc/NaCl = 4; 1 kg feed	1.5 kg capacity batch reactor
L-2	Heel + Concentrate	680	10	180	heel/conc = 5; total charge 710 g	"

Table 7 (Cont'd)

Run No.	Charge	Temp °C	Gas flows (cm^3/min) N_2	Gas flows (cm^3/min) Cl_2	Remarks	
L-3	Concentrate	650	10	135	two successive 0.5 kg batches (1 kg feed)	1.5 kg capacity batch reactor
L-4	Heel + Concentrate + NaCl	680	10	130	heel/conc/NaCl = 20/4/1; total charge 690 g	"

temperature, under the gas flows and other operating conditions specified (refer to page 39), the efficiency of chlorine utilization is high, insignificant S_xCl_y is produced, Fe_yCl_{3y} formation can be controlled and the product melt is very fluid. The curve shown can be interpreted in the following manner. At lower temperatures the chlorination efficiency is lower, thereby leaving more unchlorinated sulphides in the bath. At higher temperatures the fuming increases thus lowering the recovery of the metal chlorides into the bath. Although it is possible to recover this fume it is desirable to minimize this for a number of practical operating reasons. Two of the most important considerations are:

(1) Part of the fume may be swept into the off-gas system where it could condense in the sulphur recovery region, thus lowering sulphur grade and interfering with viscosity control.
(2) The fume may form a compact deposit which could block the off-gas lines.

Figure 10 depicts total chlorine utilization efficiencies as a function of temperature. It is apparent that the utilization efficiency reaches a plateau at ~90% at 700°C. The lower efficiency values have not been adjusted for the fact that $FeCl_3$ formed in the bath when excess chlorine was added. Since the denominator for calculating the efficiency considers $FeCl_2$ formation only, any chlorine reacted to form $FeCl_3$ in the bath would lower the apparent efficiency. The higher efficiencies shown in Fig. 10 have been calculated after correction for the fact that greater than the ideal stoichiometric amount of chlorine was indeed required (Chlorine stoichiometry ≈ 1.08).

Figure 11 illustrates that at the higher temperatures of chlorination, keeping all other parameters of operation constant, negligible S_xCl_y escapes the bath. The figure also indicates a dramatic drop in S_xCl_y evolution between 500°C and 600°C. The reason for this can only be speculated upon, with the possibilities being:

(1) a higher solubility for S_xCl_y in the bath at the higher temperature (the melt is more fluid). This would increase the reaction efficiency for MS_n plus S_xCl_y.

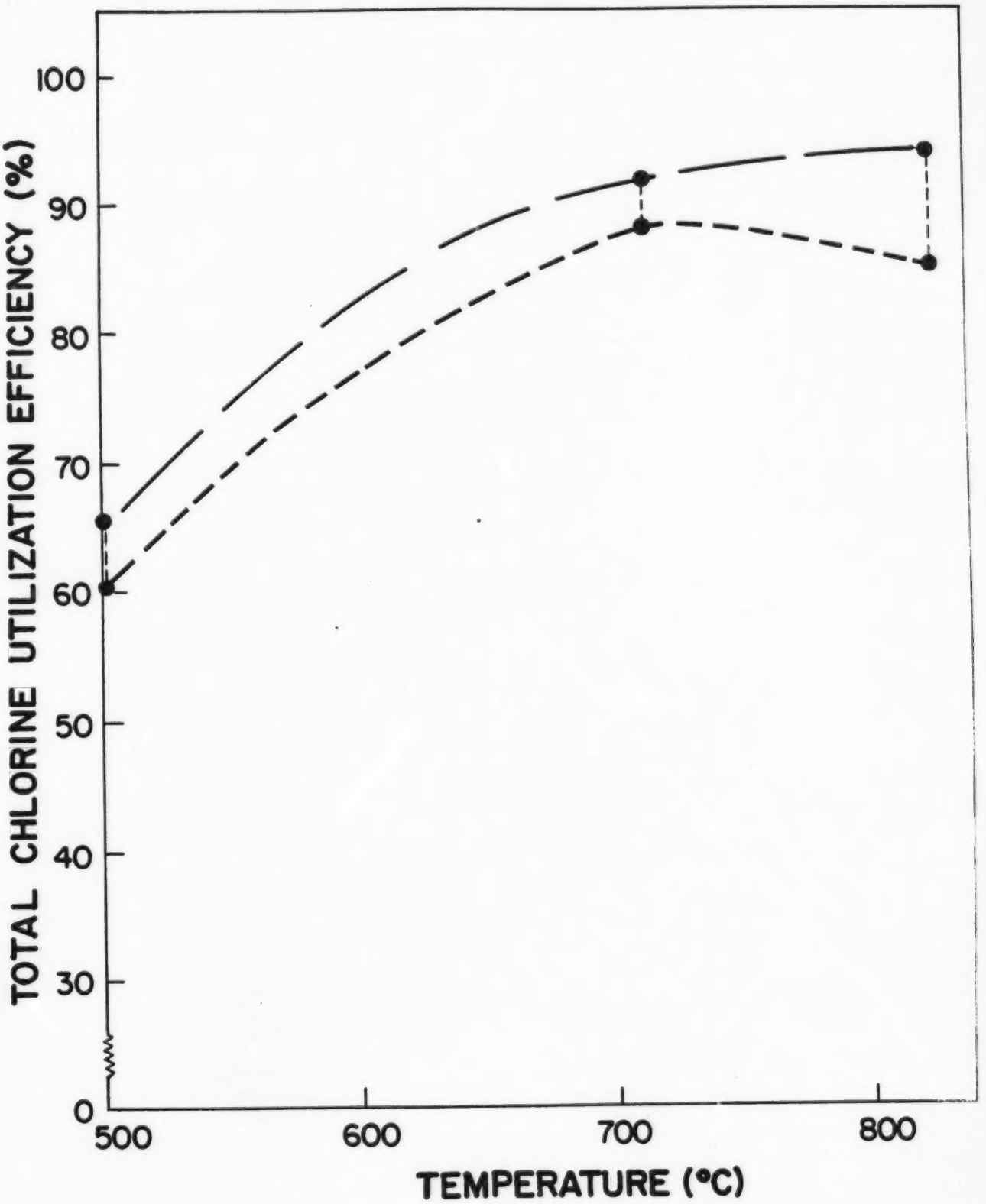
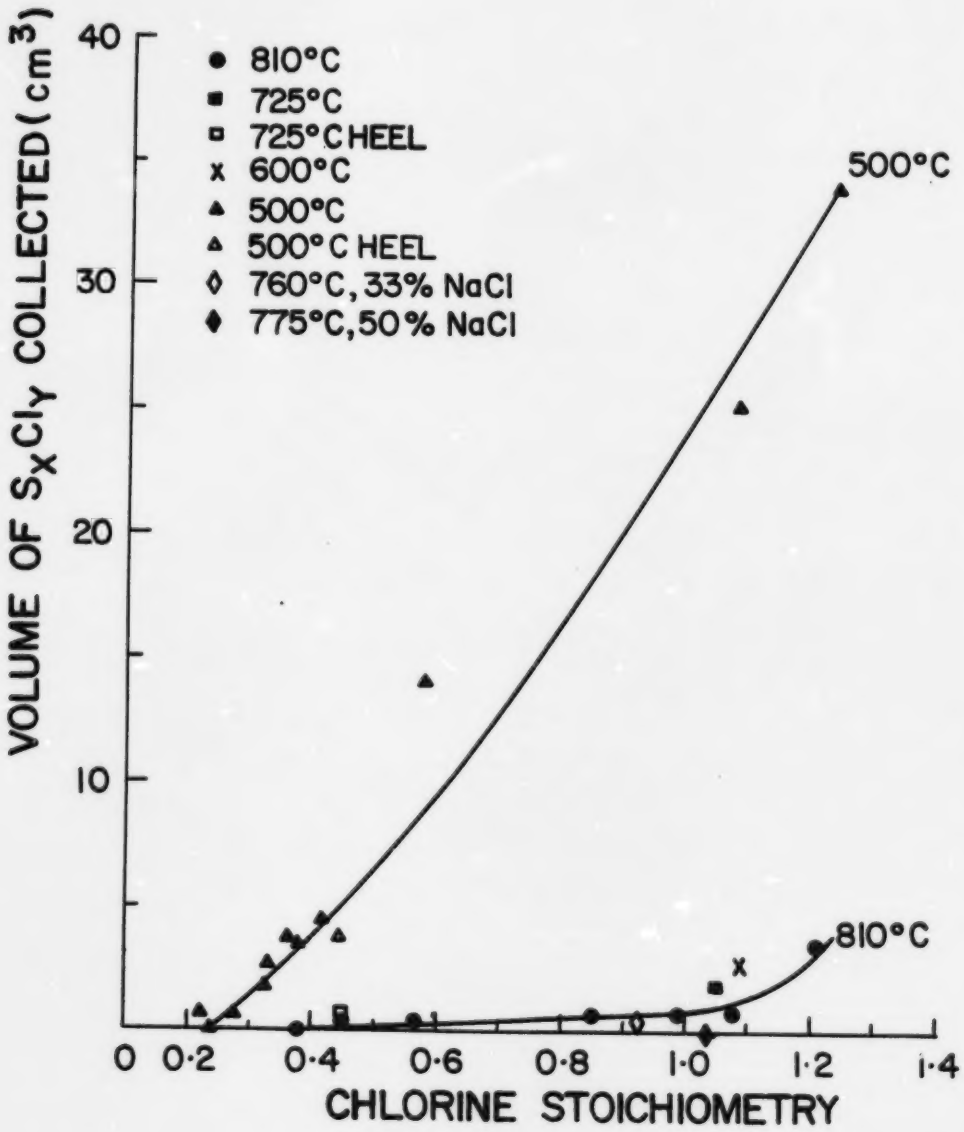


FIG 10 CHLORINE UTILIZATION EFFICIENCY AS A FUNCTION OF TEMPERATURE

FIG 11 SxCly FORMATION AS A FUNCTION OF CHLORINE STOICHIOMETRY AND TEMPERATURE



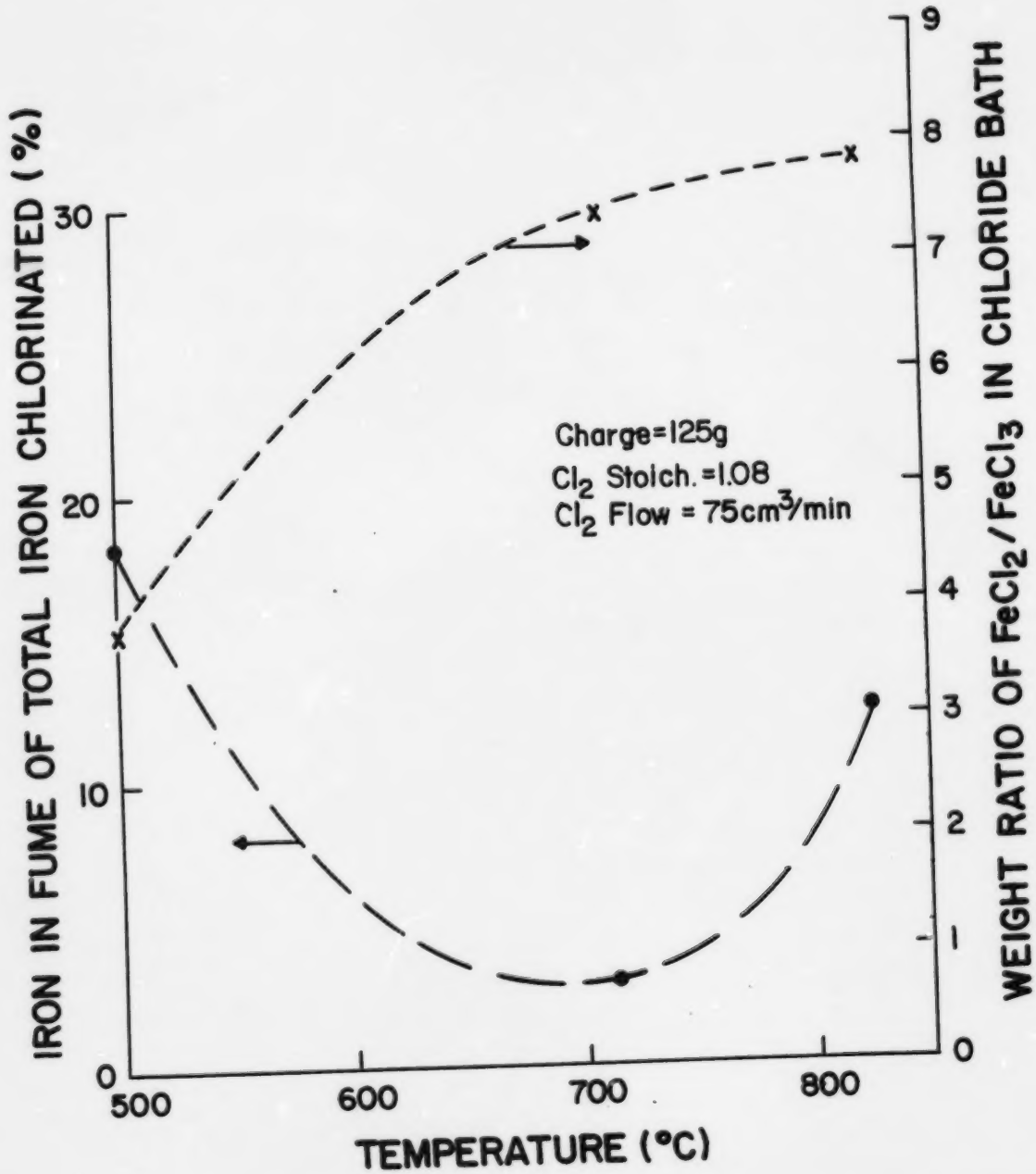
(2) a higher rate of reaction for MS_n plus S_xCl_y at the higher temperature, perhaps involving a different rate mechanism. The stability of the SCl_2 specie increases, relative to the stability of the S_2Cl_2 specie, as the temperature increases.

During the higher temperature tests S_xCl_y could be observed only after the metal sulphides had been totally converted to metal chlorides and a significant amount of $FeCl_3$ (~12-20% of the total iron as Fe^{3+}) had already formed in the bath. Essentially, free chlorine would react with the elemental sulphur in the off-gas line to form S_xCl_y which would be carried to the sulphur chlorides collector with the inert N_2 gas.

Similar reasoning is valid for the formation of $FeCl_3$ as is illustrated in Fig. 12. The diagram shows the relative quantities of Fe^{2+}/Fe^{3+} in the bath as a function of the temperature of the bath. At the lower temperatures the proportion of $FeCl_3$ can be high, while at the higher temperatures it is lower since $FeCl_3$ appears to be a good chloride donor. This comparison is valid only if all other experimental parameters were constant, especially chlorine stoichiometry. It must be emphasized that, although the analytical techniques for Fe^{2+} and Fe^{3+} have been verified, the relative proportion of Fe^{2+} and Fe^{3+} so obtained may differ from the ratios which exist in the melts. The analyses were done in filtrates obtained from leaching representative product samples.

The lower $FeCl_3$ content at higher temperatures is also partially due to the higher vapour pressure of iron chlorides. The amount of iron chloride in the fume, relative to that in the bath, appears to be lowest at ~700°C. At 680 → 700°C the efficiency of chlorine utilization was maximized under typical experimental parameters. Above perhaps 750°C the fuming rate of zinc and iron chlorides became unacceptable under the same controlled procedures. Probably the escape rate for ferric chloride from the bath exceeded its chloridizing rate within the bath. The suggested optimum small scale test conditions are the following:

FIG 12 EFFECT OF CHLORINATION TEMPERATURE ON $FeCl_3$ FORMATION



weight of concentrate and starter heel	125 g
depth of bath	10 cm
surface area of bath	5 cm^2
opening in lance; depth into bath	0.07 cm^2; 8 cm
rate of Cl_2 addition	75 cm^3/min (0.2 g/min)
total chlorine addition	1.08 x stoichiometric
rate of N_2 addition	10 cm^3/min
temperature of bath	680°C
container material	SiO_2
temperature of off-gas line	400°C
temperature of S condenser	150°C
temperature of S_xCl_y condenser	-10°C

(ii) Monitoring progress of chlorination

The progress of chlorination, with the intent of establishing the sequence of reaction of the various sulphides with chlorine, was followed by sampling the bath at regular intervals. Since the sampling was done in situ with a glass sampling tube, the solid sulphide/liquid chloride ratio in the sample might not accurately reflect the actual bath composition. Therefore to obtain a proper mass balance and to establish the weight of melt plus unreacted sulphides, and its composition, the unreacted solids (weight and composition) at any instant of time are calculated based on the assay of the chloride component. The melt weight was corrected for weight of samples removed and a new chlorine stoichiometry was established. A sample calculation is given in Appendix 1. The results are summarized in Fig. 13 and 14 as well as in Table 9, Appendix 2.

An interesting phenomenon was observed which is consistent with thermodynamic calculations. As shown in Fig. 13, at approximately 0.9 times stoichiometric chlorine, the Cu concentration in the chlorinated product dropped to a level which was close to zero. The chlorination product at this point became more fluid and it is postulated that the copper chloride served as a chloride donor to chlorinate other metal sulphides*. The increased

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* A similar phenomenon was observed for silver.

FIG 13 COPPER DISTRIBUTION IN LIQUID CHLORIDE PHASE AS A FUNCTION OF CHLORINE STOICHIOMETRY

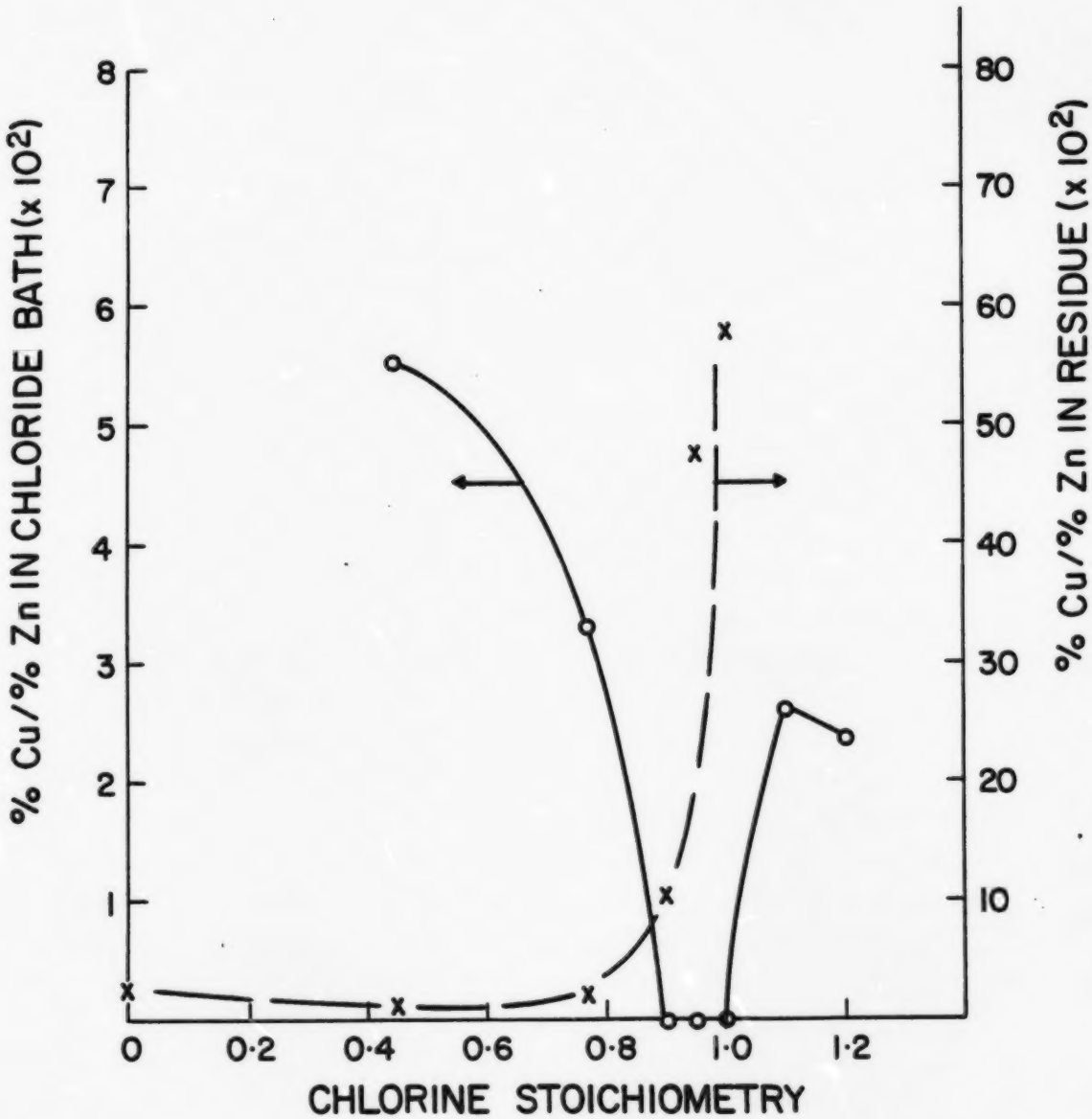
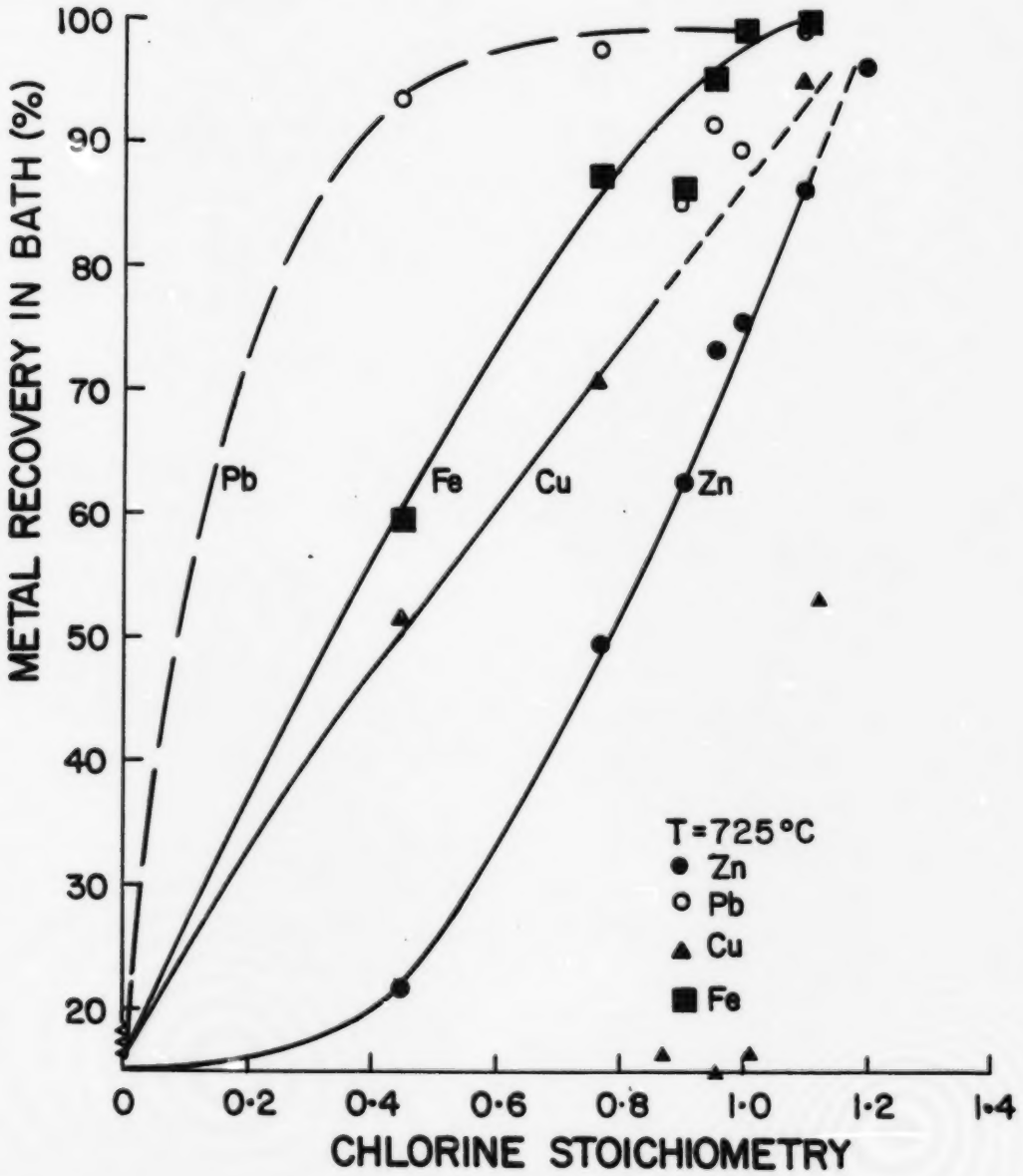


FIG 14 METALS RECOVERY IN BATH AS A FUNCTION OF CHLORINE STOICHIOMETRY



fluidity of the melt was the result of the increased metal chloride to metal sulphide ratio and, possibly, also to the increased ferric chloride to ferrous chloride ratio. Therefore there was better contact between chlorinated product and unchlorinated sulphides.

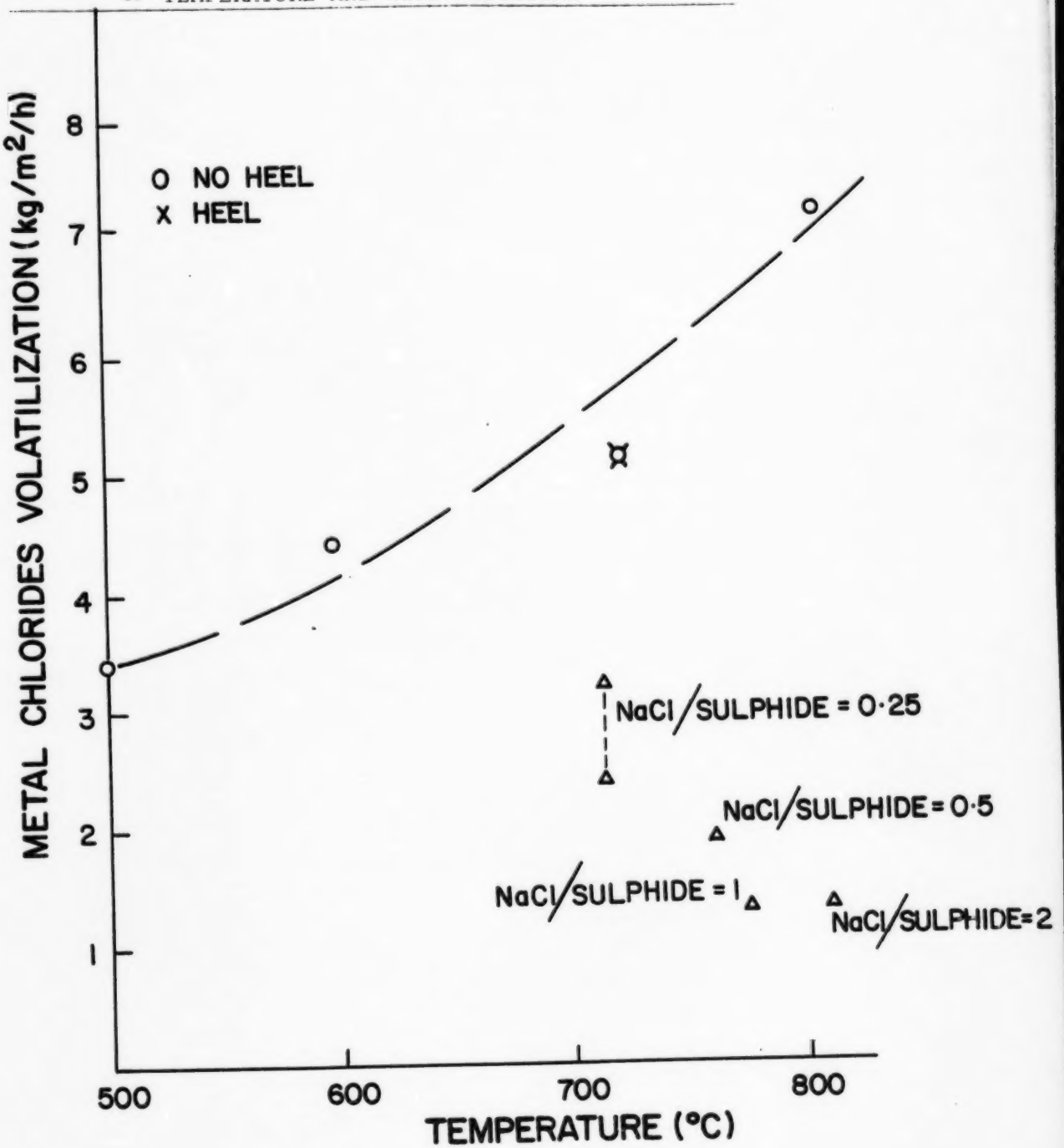
The observed sequence of chlorination of the Pb, Fe, Zn sulphides (Fig. 14) is consistent with predictions (Fig. 1). The apparent anomaly in regard to copper may be due to its presence in the concentrate primarily as chalcopyrite ($CuFeS_2$). Thermodynamic considerations indicate that Cu_2S would be expected to chlorinate last when considering only the non-complexed sulphides of Pb, Fe, Zn and Cu. A drop in the Pb concentration at about 0.8 times stoichiometry is attributed to a possible sampling error introduced due to $PbCl_2$ precipitation from solution.

(iii) Effect of NaCl additions

In order to decrease the quantity of $ZnCl_2$ fumed during chlorination, various quantities of NaCl were added with the reactor charge. The chlorination procedure was identical to that used during chlorination without NaCl. All melts were very fluid, as would be expected with these chloride mixtures. During chlorination, the chlorine utilization efficiencies were high and no sulphur chlorides appeared in the off-gas system. The Fe^{2+}/Fe^{3+} equilibrium was shifted in the presence of NaCl, with the salt having a stabilizing effect on Fe^{3+}. This feature is desirable during the chlorination step. However, the effect is undesirable for the proposed overall flow sheet since, as subsequent tests verified, the iron could not be readily removed from the bath by chlorination/vaporization of Fe_yCl_{3y} from the NaCl-containing bath. This in turn results in a high iron content in the final product which is not acceptable for the hydrometallurgical processing component of the flowsheet.

The effect of NaCl in lowering the weight of metal chlorides volatilized (extrapolated to kg of metal chlorides volatilized/m^2 of bath/h of operation) is illustrated in Fig. 15. The effect is significant. When the dilution of the metal chlorides by the NaCl is taken into account i.e., their activity is lowered due to lower concentration, then it becomes apparent that no strong complexes are formed since P_i is proportional to X_i, where P_i = partial pressure of component i and X_i = mole fraction of component i. That is, there is no significant lowering of the activities beyond the dilution effect.

FIG 15 METAL CHLORIDES VOLATILIZATION AS A FUNCTION OF TEMPERATURE AND NaCl ADDITIONS



The results are represented in a different manner in Fig. 16, which illustrates more clearly the effect of NaCl on volatilization of metal chlorides at a constant chlorination temperature of 650°C. At a NaCl/sulphide ratio of 0.25 the volatilization rate approaches zero at chlorine flows of 75 cm^3/min, since the Fe_yCl_{3y} species and the $ZnCl_2$ were both stabilized due to the dilution effect by NaCl. When the chlorine injection rate was increased to 300 cm^3/min, the fuming rate, as expected, increased due to the higher turbulence and sulphur evolution rate.

(iv) Mass balances and distribution of elements

Mass balance calculations were carried out on results from all tests. The importance of doing these calculations can not be overemphasized. Examples are given in Tables 9 to 13, Appendix 2.

The decision was made to obtain samples from various locations in the circuit to assist in designing equipment for future tests and to obtain some preliminary indication as to the possible distribution of elements in a commercial chlorination reactor.

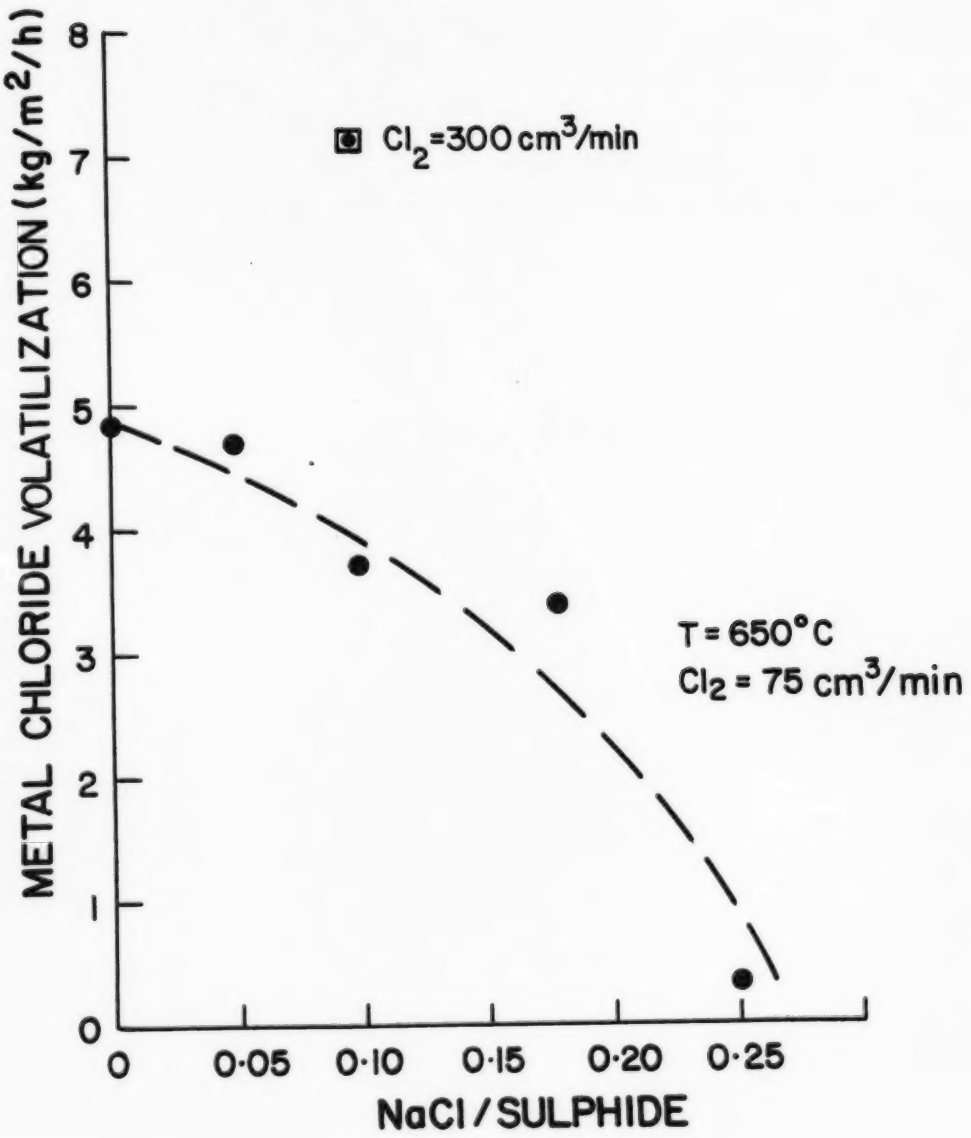
The accountability of all elements, as determined from the vertical summation of per cent distribution of the element, can be seen to be >95% in all cases. The percent distribution of each element in each sample is a function of the quantity of that element in the input materials i.e.,

$$\% \text{ Dist'b} = \frac{\text{wt element in sample}}{\text{wt element in head}} \times 100$$

Sulphur balances were the most difficult to close when considering the analyses from initial tests. A substantial (~5%) amount of sulphur was often dissolved in the caustic scrubber solution. Some of this sulphur could have been carried to the scrubber as SO_2 which may have formed as a result of reaction with the oxygen in some gangue materials or in the sulphate. Furthermore, S_xCl_y vapour pressure is high at normal temperatures, and sulphur can be difficult to condense when in the form of an aerosol. Aerosol entrapment is a function of condenser design and efficiency. Elemental sulphur also has a high solubility in caustic solutions.

In the tables, the horizontal summation of compositions of the various samples served as a check on the accuracy of the chemical analysis.

FIG 16 METAL CHLORIDE VOLATILIZATION AS A FUNCTION OF NaCl CONTENT IN BATH



Combining the results from a number of experiments, a typical mass balance has been compiled in Table 8. It is proposed that the chlorination temperature should be 680°C and that the final melt will be at 550°C. Zinc chloride fume is, therefore, assumed to condense back into the downstream bath in a commercial chlorinator (Fig. 17). The mass balance for the minerals beneficiation circuit is also included in Table 8. The basis for the chlorination mass balance is 100 units of concentrate with the percent distribution of all elements in the feed to the chlorinator taken as 100. The minerals beneficiation circuit mass balance has the ore as head equal to 100. After chlorination of 100 units of concentrate, 125 units of molten chloride product are formed with the recovery of all metals in the bath being high. The fume contains 4% of the total zinc present (assuming the proposed temperature drop in the downstream region of the bath). This fume should, in a commercial operation, be recycled to the chlorinator since it probably contains substantial sulphur. The sulphur is in both the elemental form and as metal sulphides dust. The analysis of the sulphur product shown in Table 8 is that of a particularly good fraction obtained within the mid-point range of a test. The metals concentration in the sulphur was low. The highest concentrations of impurities in this case were chloride (0.6%) and arsenic (0.4%). More typically, the sulphur product analyzed 95% S.

Some of the other elements which have been monitored and for which a preliminary distribution has been established are given below:

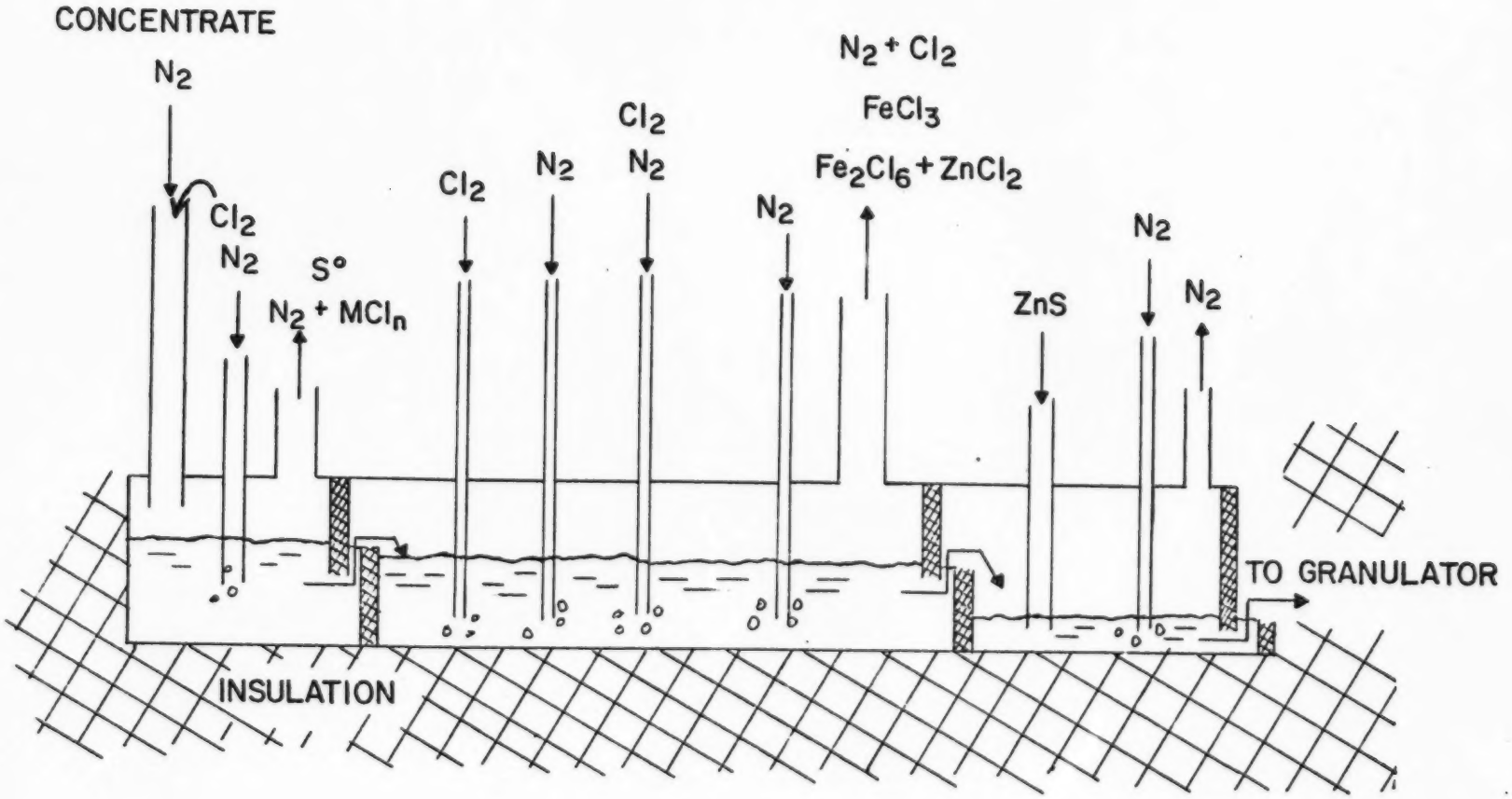
Element	Concentration in bath (%)	Distribution into bath (%)*
As	0.04 → <0.005	16 → <2
Co	0.01 → 0.001	100 → 10
Sb	<0.0005	<1
Cd	0.001	2
Ni	0.0003	10

* As a function of input concentration

Table 8 - Mass balance for processing circuit (Optimized summary of test programs)

	Weight		Zn	Pb	Cu	Fe	Ag	S	Wt % (total)
Minerals Beneficiation									
Ore	368	wt %	8.5	3.2	0.2	29.6	0.009	38.0	79.5
		Dist'b	100	100	100	100	100	100	
Concentrate	100	wt %	30.1	9.8	0.7	20.2	0.03	37.0	97.8
		Dist'b	96	85	78	19	80	26	
Tailings	268	wt %	0.4	0.8	0.1	33.1	0.003	38.4	72.8
		Dist'b	4	15	22	81	20	74	
Chlorinator									
Concentrate	100	wt %	30.1	9.8	0.7	20.2	0.03	37.0	97.8
		Dist'b	100	100	100	100	100	100	
Chlorinator Product (Excluding Recycle)	123	wt %	23.1	7.9	0.6	16.3	0.03	<0.6	~48.5
		Dist'b	95	99	100	99	100	<2	
Chlorinator Condensate (Recycled)	5	wt %	31.9	1.3	<0.5	3.6		19.5	~56.8
		Dist'b	4	<1	<0.1	1		3	
Sulphur Product	36	wt %	<0.1	<0.01		<0.1		98.8	~99.0
		Dist'b	<0.1	<0.1		<0.02		97	

FIG 17 CONCEPTUAL DESIGN OF REACTOR

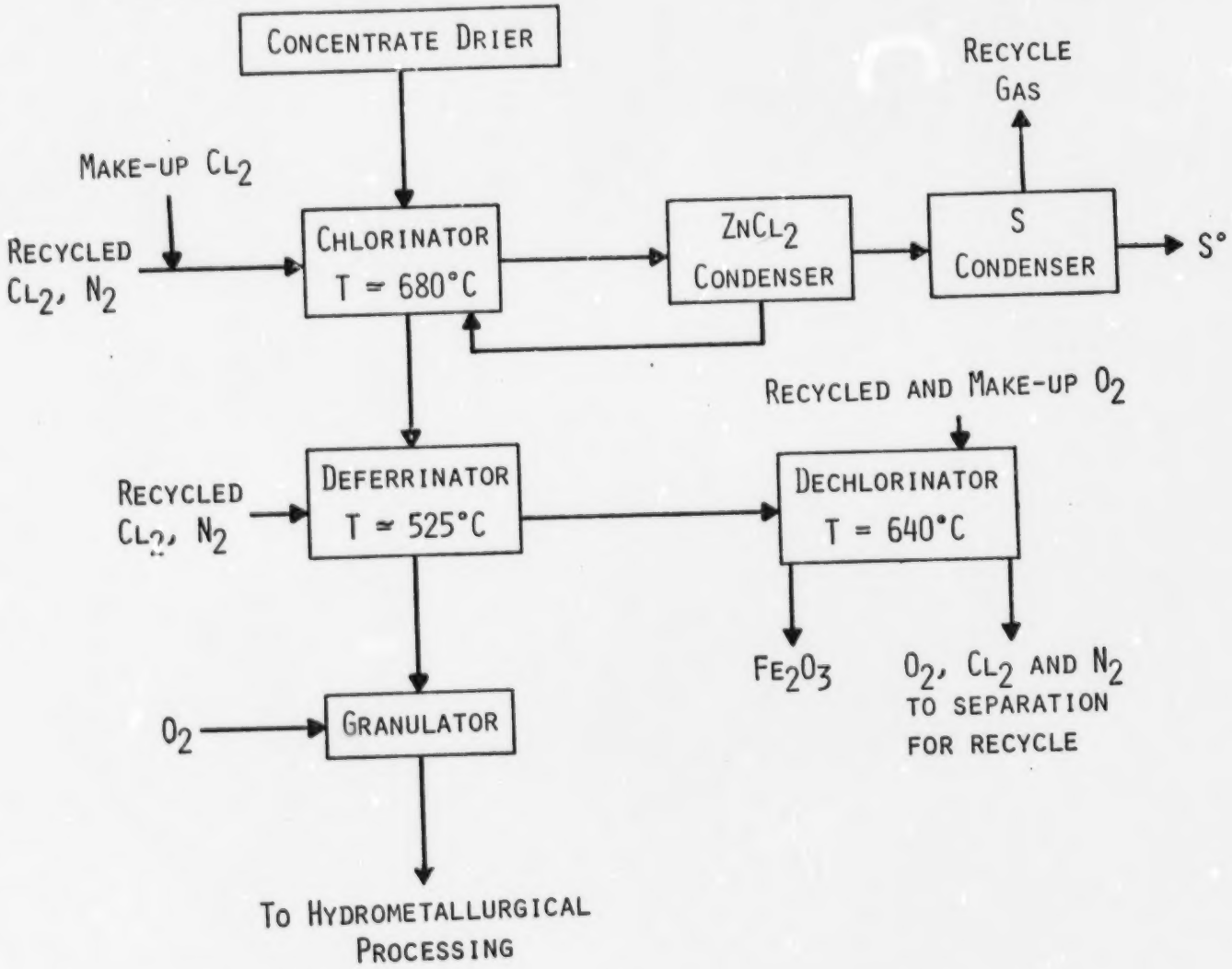


COMMERCIAL PYROMETALLURGICAL PROCESSING CIRCUIT

Based on small-scale batch chlorination tests and on knowledge of chlorine / metal chloride / metal sulphide systems, a conceptual flowsheet for the pyrometallurgical treatment of bulk concentrate has been developed and is shown in Fig. 18. The main pyrometallurgical unit operations in the processing flowsheet, following minerals beneficiation, are chlorination, deferrination (iron removal) and dechlorination (combustion of ferric chlorides in air or oxygen). The primary products from the first two operations are gaseous sulphur (1st), gaseous Fe_yCl_{3y} (2nd) and low iron content molten chlorides (combined operations). Preliminary granulation tests of the molten chloride in oxygen have proven that the iron content of the bath can be lowered further. The granulated product can be leached and processed hydrometallurgically. In the dechlorination step the Fe_yCl_{3y} is oxidized to Fe_2O_3 and Cl_2 gas which is recycled.

Figure 17 shows one possible layout for a commercial reactor. The circuit consists of 3 unit operations, namely a sulphide chlorinator, a deferrinator and a high temperature cementator. The conceptual reactor is essentially a refractory-lined trough with the gas seal between the compartments being made by overflow, underflow weirs. The transport of the fluid chlorinated product is by gravity. The restriction on the conceptual design is that relatively fluid melts must be maintained and that gangue materials be of a reasonably low concentration so that a mush is not produced. Sulphide concentrate, chlorine gas and some nitrogen gas are fed into the first compartment. If the sulphide is fed to the top or into the bath, the chlorine can be injected via a submerged lance or through tuyeres. However, recent work done at Ontario Research Foundation (12) suggests that the preferred mode of reacting the sulphide and chlorine would be in a solids/gas "flash" burner. It is proposed that approximately 90-95% of the conversion be conducted by employing the "flash" burner, with the remaining 10% being done by submerged-lance injection of chlorine. The outflows from this chlorination step are molten metal chloride, sulphur gas, some metal chloride fume, nitrogen gas and some chlorine gas. The metal chlorides should be recycled to the reactor. The second unit operation is the deferrination, where excess chlorine and some nitrogen gas are sparged into the melt. The chlorine oxidizes the $FeCl_2$ to $FeCl_3$ and/or Fe_2Cl_6 which have a relatively high vapour pressure and are

FIG 18 PYROMETALLURGICAL COMPONENT OF PROCESSING FLOWSHEET



vapourized from the bath. The nitrogen serves as a carrier gas. From preliminary tests (9) it appears that the rate-controlling step in the deferrinator is the evolution of the iron chlorides from the bath and that the rate of $FeCl_2$ oxidation is rapid. The N_2 gas purging shifts the Fe^{2+}/Fe^{3+} equilibrium by removing the Fe_yCl_{3y} (Le Chatelier principle). The outputs from this unit operation are gaseous Fe_yCl_{3y}, excess chlorine gas, nitrogen gas and a low iron (0.8 - 1.2%) molten chloride. Chlorine stoichiometry of 2X theoretical was required to convert $FeCl_2$ to $FeCl_3$ under non-optimized conditions.

The third proposed unit operation is not essential to the flowsheet but does suggest an interesting concept. If ZnS is added to the bath it is expected to be chlorinated by the iron, silver and copper chlorides which in turn exchange to accept the sulphur. Therefore after leaching of the product from the cementator a Cu-Ag-Fe-S concentrate could result. A few tests aimed at confirming this concept are encouraging. The leach liquors would be processed hydrometallurgically. Alternatively, the output (chloride and sulphide) from the cementator could be granulated in air or oxygen before entering the hydrometallurgical circuit. The product from the deferrinator could also be leached directly.

The description of a conceptual chlorination/deferrination/dechlorination flowsheet and some design parameters have been presented previously (9).

CONCLUSIONS AND RECOMMENDATIONS

A pyrometallurgical chlorination process has been developed for the treatment of complex sulphide ores. Specifically the following items have been verified:

(1) Brunswick bulk concentrate can be readily chlorinated in the temperature range 500°C to 850°C with the optimum temperature being approximately 675°C.
(2) Chlorine utilization efficiency is high.
(3) The extraction of the metals into the melts can be >95%.
(4) The resulting chloride melts are very fluid, can be contained and flow readily.

(5) There is no apparent build-up of inert gangue materials. These are found to be dispersed throughout the bath.

(6) Good quality sulphur (>98%) can be produced.

(7) Production of Fe_yCl_{3y} and S_xCl_y can be minimized.

(8) Fuming from the bath can be controlled. However the practicality of adding NaCl to achieve this is questionable, especially if the process relies on deferrination of the product by fuming of Fe_yCl_{3y}.

(9) The process is autogenous, even when heat losses of the order of 10% are assumed.

(10) The process could be applicable to the extraction of valuable components from other complex sulphide concentrates, and could be considered for conventional concentrates in cases where sulphuric acid cannot be marketed and SO_2 emissions must be controlled.

Overall the results from the small scale tests have been very encouraging and as a result the following recommendations are made:

(1) The high temperature chlorination concept be tested on a larger scale with continuous feeding of sulphide concentrate and chlorine. A limited amount of work has already been done at CANMET and is the subject of a future progress report.

(2) The flash chlorination concept be tested further. Preliminary work at Ontario Research Foundation has shown that the rates of reaction between the metal sulphides and chlorine are rapid. This was predicted from the small scale submerged-lance tests.

(3) Studies be undertaken to develop a practical process for dechlorinating Fe_yCl_{3y}.

(4) The high temperature chlorination concept be tested on other concentrates.

(5) Conduct studies to further develop the hydrometallurgical component of the flowsheet, particularly with respect to lead/silver recovery and the efficiency of chlorine recycle.

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APPENDIX 1

MASS BALANCES

APPENDIX 1

MASS BALANCES

(1) Sample calculations for theoretical mass balance

1. Theoretical chlorine requirement to convert metal chlorides to metal sulphides

Reactions considered:

$2ZnS + 2Cl_2 \rightarrow 2ZnCl_2 + S_2$

$2PbS + 2Cl_2 \rightarrow 2PbCl_2 + S_2$

$2Cu_2S + 2Cl_2 \rightarrow 4CuCl + S_2$

$2FeS + 2Cl_2 \rightarrow 2FeCl_2 + S_2$

$FeS_2 + Cl_2 \rightarrow FeCl_2 + S_2$

$2Ag_2S + 2Cl_2 \rightarrow 4AgCl + S_2$

Basis of calculation:

100 g of concentrate containing (wt %):

29.9 Zn
9.5 Pb
0.7 Cu
19.9 Fe
36.6 S
0.024 Ag

The concentrations of iron as FeS and FeS_2 are established by:

a) total S = S associated with (Zn + Pb + Cu + Ag)

$$+ \frac{\text{M.W. of S}}{\text{M.W. of Fe}} \times \text{wt Fe as FeS} + 2\frac{\text{(M.W. of S)}}{\text{M.W. of Fe}} \times \text{wt Fe as } FeS_2$$

b) total Fe = Fe as FeS_2 + Fe as FeS

(2) Sample mass balance calculation for Test No. 11 (Refer to Table 9, Appendix 2)

The weight % of the metals in the chlorinated product is determined from the chemical analysis of the sample using the weight of the soluble chloride as the denominator, i.e.,

$$\text{wt \%} = \frac{\text{wt metal in sample}}{\text{wt sample - wt sample residue}} \times 100$$

The weight % of chlorine in the chloride product is calculated assuming that the sum of the concentration of elements of interest is 100%, i.e.,

$$\text{wt \% Cl} = 100 - \Sigma \text{ \% metals}$$

This value can be checked by calculating the appropriate amount of chloride for each one of the metals and summing these amounts.

Using blow 1 as an illustration, at this point of chlorination the weight of chlorine added to the system is 37.7 grams. Assuming 95% chlorine utilization efficiency and correcting for fume escape the actual chlorine in the bath will be lower. The fuming is approximated to be distributed linearly over the whole test with the analysis at each instant of time being the same as the final fume composition. Thus at a chlorine input of 37.7 grams, 43% of the total fume would have been produced, or 8.4 grams, of which 5.1 grams are chlorine. Therefore, the weight of chlorine in the bath, including the sample taken for analysis is

$$(37.7 \times 0.95) - 5.1 = 30.7 \text{ grams}$$

This 30.7 g is equivalent to 48.7% of the chlorinated product at this specific instant of time. Thus the total weight of chlorinated product can be calculated as

$$\frac{30.7}{0.487} = 63.04 \text{ g}$$

The total amount of each metal can be calculated by (weight of chlorinated product x % metal in product) + weight of element in fume. Thus, for zinc, weight = 7.69 (in melt) + 1.22 (in fume) = 8.91 g. Repeating the procedure for all elements the total chlorinated product weight after blow 1 is 76.6 g. The weight per cent of zinc, for example, can thus be calculated as $\frac{8.91}{76.6} \times 100 = 11.6$.

The conversion of each metal can be established as a function of the metal input in the head.

In order to determine the weight of unchlorinated sulphides, again it is necessary to rely on the mass balances since the solids in the draw sample were not of representative weight. For example, the quantity of unchlorinated zinc remaining as the sulphide is

40.4 (zinc in head) - 8.9 (chlorinated) = 31.5 g

Summing all of the elements, including sulphur which is calculated from stoichiometry, the total weight of unchlorinated sulphides at the end of blow 1 is 69 g. In calculating the sulphur associated with the metals in the unchlorinated product 75% of the iron is assumed to be as FeS and 25% as FeS_2. The rationale for this assumption is that some thermal decomposition of the FeS_2 to FeS and S would take place. The calculation for concentration and proportion unchlorinated as a function of input is obvious.

APPENDIX 2

CHLORINATION TEST RESULTS

APPENDIX 2

CHLORINATION TEST RESULTS

Table 9 - Chlorination Test No. 11[1,2]

Chlorine stoichiometry[2]		Weight (g)		Zn	Pb	Cu	Fe	Ag	S	Cl	Wt % (total)
	Concentrate	135	wt %	29.9	9.5	0.7	19.9	0.023	36.6		96.6
			dist'n %	100	100	100	100	100	100		
	Chlorine	87.7	wt %							100	
			dist'n %							100	
0.44	Chlorides	77	wt %	11.6	13.7	0.6	20.7			53.4	100
			rec'y %	22	82	47	59			34.4	
	Concentrate[3]	69	wt %	46.3	3.3	0.7	16.2		33.5		100
			dist'n %	79	18	53	41		47[4]		
0.76	Chlorides	113	wt %	16.2	9.6	0.6	20.3			53.3	100
			rec'y %	45	84	67	85			61	
	Concentrate[3]	41	wt %	53.5	6.1	0.8	7.6		30.3		98.3
			dist'n %	54	16	33	15		25[4]		
0.91	Chlorides	132	wt %	19.2	8.0	<0.1	19.5			53.3	100
			rec'y %	62	83	5	96			61	
	Concentrate[3]	29	wt %	53.8	7.6	3.1	4.1		30.0		98.6
			dist'n %	38	17	95	5		18[4]		
0.95	Chlorides	139	wt %	20.2	7.9	<0.1	19.4				
			rec'y %	70	86	<4	100				

(1) Batch chlorination, temperature = 725°C, Cl_2 flow rate = 72 cm^3/min @ 25°C (0.2 g/min), chlorination time = 7.1 h.

(2) Data based on mass balance calculations, draw samples and chlorine consumption; 95% chlorine utilization efficiency assumed. Stoichiometry correlated for weight decrease of bath.

(3) Calculated compositions and weights. Draw samples do not give representative solid sulphide sample.

(4) 75% thermal decomposition of FeS_2 to FeS and S assumed.

Table 9 (Cont'd)

Chlorine stoichiometry[2]		Weight (g)		Zn	Pb	Cu	Fe	Ag	S	Cl	Wt % (total)
	Concentrate[3]	23	wt %	54.5	7.8	>3.9	0		27.4		>93.6
			dist'n %	31	14	>96			13[4]		
1.00	Chlorides	144	wt %	20.6	7.2	<0.1	19.3			53.1	100.2
			rec'y %	74	81	<4	100			87	
	Concentrate[3]	22	wt %	48.5	11.0	>4.0	0		26.4		>89.9
			dist'n %	26	19	>9.6	0		12[4]		
1.10	Chlorides	153	wt %	21.7	7.7	0.3	18.1			53.2	101
			rec'y %	82	92	53	100			93	
	Concentrate[3]	14	wt %	51.4	7.1	3.1	0		30.0		94.3
			dist'n %	18	8	47	0		9[4]		
1.20	Chlorides	165	wt %	21.6	7.5	0.5	17.6			51.9	99.1
			rec'y %	88	97	95	100			97	
	Unaccounted (losses/fume)		dist'n %	12	3	5	0				

(2) Data based on mass balance calculations, draw samples and chlorine consumption; 95% chlorine utilization efficiency assumed. Stoichiometry correlated for weight decrease of bath.

(3) Calculated compositions and weights. Draw samples do not give representative solid sulphide sample.

(4) 75% thermal decomposition of FeS_2 to FeS and S assumed.

Table 10 - Chlorination Test No. 2[1]

Charge	Weight (g)	Weight (%)		Zn	Pb	Cu	Fe	Ag	S	As	Cl	Co	Wt % (total)
Concentrate	93.2	60.6	wt %	29.9	9.5	0.7	19.9	0.024	36.6	0.24		0.01	96.9
			dist'n	100	100	100	100	100	100	100		100	
Chlorine	60.7	39.4	wt %								100		
	153.9	100.0	dist'n								100		
Products													
Bath	100.2	65.1	wt %	22.6	8.4	0.6	17.4	0.02	0.9	0.04	50.0	0.01	100
			dist'n	81.2	94.7	92.2	94.2	91	2.5	16	82.4	100	
Cold top, off-gas lines, lance, reactor walls	16.4	10.7	wt %	20.7	1.0	0.03	3.1	<0.01	25.5		36.2		86.5
			dist'n	12.2	1.9	0.8	2.7	<7	12.3		9.8		
Sulphur collector	22.1	14.4	wt %						98		1.5		99.5
			dist'n %						63.4		0.4		
Sulphur chloride[2] collector	2.6	1.7	wt %						58		42		100
			dist'n %						4.4		1.8		
Scrubbers	4.0	2.6	wt %	10.6			0.2		66.4		22.7		99.9
			dist'n %	1.5			0.05		7.7		1.5		
Unaccounted	8.6	5.6	dist'n %	5.1	3.4	7.0	3.1	>2	9.7		4.1	0	

(1) Batch chlorination, temperature ~725°C, Cl_2 flow rate = 70 cm^3/min @ 25°C (0.2 g/min), chlorination time = 5.55 h.

(2) Assume liquid composition as S_2Cl_2. Formed at end of test.

Table 11 - Chlorination Test No. 12[1]

Charge	Weight (g)	Weight (%)		Zn	Pb	Cu	Fe	Ag	S	As	Cl	Wt % (total)
Heel	81.7	54.5	wt %	23.9	7.9	0.55	15.4				49.2	97.0
			dist'n %	61.4	62.2	60.8	60.7				59.6	
Concentrate	40.9	27.3	wt %	29.9	9.5	0.7	19.9	0.024	36.6	0.23		96.8
			dist'n %	38.6	37.8	39.2	39.3	100	100	100		
Chlorine	27.2	18.2	wt %								100	
	149.8	100.0	dist'n %								40.4	
Products												
Bath												
(a) Chlorinated	122.0	81.4	wt %	23.7	9.1	0.5	16.6[2]				53.3	103.2
			dist'n %	91.2	100	89.5	97.9				96.5	
(b) Unchlorinated	0.4	0.3										
Reactor walls,	5.8	3.9	wt %	25.5	2.0	0.1	8.3		14.6		36.7	87.2
lance, thermowell			dist'n %	4.7	1.1	0.6	2.3		5.7		3.2	
Sulphur collector	13.1	8.7	wt %	0.04	<0.01		0.02		99.8	<0.05	12 ppm	99.9
			dist'n %	0.02	<0.01		0.01		89.4	<3		
Scrubbers	3.3	2.2	wt %	<0.03					30.6		69.4	100
			dist'n %	<0.003					6.8		3.4	
Unaccounted	1.4	0.9	dist'n %	4.1		9.9						

(1) Batch chlorination with heel, temperature = 725°C, Cl_2 flow rate = 83 cm^3/min @ 25°C (0.24 g/min), chlorination time = 1.9 hours, heel/concentrate = 2/1.

(2) Fe^{3+} = 33.5%

Table 12 - Chlorination Test No. 24(1)

Charge	Weight (g)	Weight (%)		Zn	Pb	Cu	Fe	Ag	S	Cl	Na	Wt % (total)
Concentrate	120	52.3	wt %	29.5	9.31	0.64	19.7	0.027	37.1			96.3
			dist'n %	100	100	100	100	100	100			
NaCl	30	13.1	wt %							60.7	39.3	100
										18.6	100	
Chlorine	79.6	34.7	wt %							100		
	229.6	100.0	dist'n %							81.4		
Products												
Bath												
(a) Chlorinated (incl. NaCl)	171.3	74.6	wt %	18.9	6.2	0.43	12.1	0.016		50.6	6.9	95.2
			dist'n %	92.0	96.2	96.5	88.3	87.5		88.7	100	
(b) Unchlorinated	1.0	0.4										
Cold top, off-gas lines	7.9	3.4	wt %	10.3	1.0	0.1	20.8		16.5	50.6		99.3
			dist'n %	2.3	0.7	0.4	6.9		2.9	4.1		
Sulphur collector	36.4	15.9	wt %	0.03			0.11		94.0	6.0		100.1
			dist'n %	0.03			0.2		76.9	2.3		
Sulphur chloride collector	3.0	1.3	wt %						46.7	53.3		100
			dist'n %						3.1	1.6		
Scrubbers	1.5	0.7	wt %	0.001			0.002		53.0	47.0		100
			dist'n %	0.001			0.002		1.8	0.7		
Unaccounted	8.5	3.7	dist'n %	5.7	3.1	3.1	4.6	12.5	15.3	2.6		

(1) Batch chlorination with NaCl, temperature = 650°C, Cl_2 flowrate = 70 cm^3/min @ 25°C (0.2 g/min), chlorination time - 6.5 h, NaCl/sulphide = 1/4.

Table 13 - Chlorination Test No. 25[1]

Charge	Weight (g)	Weight (%)		Zn	Pb	Cu	Fe	Ag	S	Cl	Na	Wt % (total)
Heel	100	56.9	wt %	18.9	6.2	0.43	12.1	0.016		50.6	6.9	95.1
			dist'n %	61.4	62.7	62.3	60.5	59.3		61.4	63.9	
Concentrate	40	22.8	wt %	29.5	9.3	0.64	19.7	0.027	37.1			96.2
			dist'n %	38.6	37.3	37.7	39.5	40.7	100			
NaCl	10	5.7	wt %							60.7	39.3	100
			dist'n %							7.4	36.1	
Chlorine	25.7	14.6	wt %							100		
	175.7	100.0	dist'n %							31.2		
Products												
Bath												
(a) Chlorinated	157.5	90.1	wt %	18.1	6.5	0.44	12.5[2]	0.01		50.1	6.9	94.6
			dist'n %	92.5	>100	>100	98.5	63.0		95.5		
(b) Unchlorinated	0.8	0.5										
Cold top, off-gas	4.7	2.7	wt %	17.7			10.9		29.8	40.4		98.8
lines			dist'n %	2.7			2.6		9.5	2.3		
Sulphur collector	10.2	15.8	wt %	0.05			0.09		97.0	2.9		100
			dist'n %	0.23			0.04		66.9	0.4		
Sulphur chloride	1.2	0.7	wt %						47.0	53.0		100
			dist'n %						4.0	0.7		
Scrubbers	1.5	0.9	wt %						6.7	93.3		100
			dist'n %						0.7	1.7		
Unaccounted	0	0	dist'n %	4.6	0	0	0	37.0	18.9	0		

(1) Batch chlorination with heel and NaCl, temperature = 650°C, chlorine flow rate = 70 cm^3/min @ 25°C (0.2 g/min), chlorination time = 2.1 h, NaCl/sulphide = 1/4.

(2) Assume 20% Fe^{3+}